

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of Date: May 15, 2008  
Applicants: Bednorz et al. Docket: YO987-074BZ  
Serial No.: 08/479,810 Group Art Unit: 1751  
Filed: June 7, 1995 Examiner: M. Kopec  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION  
Commissioner for Patents  
United States Patent and Trademark Office  
P.O. Box 1450  
Alexandria, VA 22313-1450

**APPEAL BRIEF  
PART IX**

**CFR 37 § 41.37(c) (1) (ix)  
SECTION 1**

**VOLUME 5**

**Part 2**

**BRIEF ATTACHMENTS AM TO AW**

Respectfully submitted,

/Daniel P Morris/

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**BRIEF ATTACHMENT AM**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

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For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
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Date: April 14, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**SIXTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated July 28, 2004, please consider the  
following:

# RECEIPT

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

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For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents  
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### AFFIDAVIT UNDER 37 C.F.R. 1.132

Sir:

I, Thomas M. Shaw, being duly sworn, do hereby depose and state:

1. I received a B. S. degree in Metallurgy from the University of Liverpool, Liverpool, England and a M. S. and a Ph.D. degree in Material Science (1981) from the University of California, Berkeley.
2. I refer to Attachments A to Z and AA herein which were submitted in a separate paper designated as "FIRST SUPPLEMENTAL AMENDMENT" in response to the Office Action dated July 28, 2004. I also refer to Attachments AB to AG which were submitted in a separate paper designated as "THIRD SUPPLEMENTAL AMENDMENT" in response to the Office Action dated July 28, 2004.
3. I have worked as a postdoctoral researcher in the Material Science Department of Cornell University from 1981-1982. I have worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1984 to the present.

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3. I have worked as a postdoctoral researcher in the Material Science Department of Cornell University form 1981-1982. I have worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1984 to the present.

4. I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

5. My resume and list of publications is in Attachment 1 included with this affidavit.

6. This affidavit is in addition to my affidavit dated December 15, 1998. I have reviewed the above-identified patent application (Bednorz-Mueller application) and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity in a material having a  $T_c \geq 26^{\circ}\text{K}$  and that subsequent developments in this field have been based on this work.

7. All the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner, have similar magnetic properties, and have similar structural properties.

8. Once a person of skill in the art knows of a specific type of composition described in the Bednorz-Mueller application which is superconducting at greater than or equal to  $26^{\circ}\text{K}$ , such a person of skill in the art, using the techniques described in the Bednorz-Mueller application, which includes all principles of ceramic fabrication known at the time the application was initially filed, can make the compositions encompassed by the claims of the Bednorz-Mueller application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art of the fabrication of ceramic materials. This is why the work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period after their discovery. Bednorz and Mueller's discovery was first reported in Z. Phys. B 64 page 189-193 (1996).

9. The techniques for placing a superconductive composition into a superconducting state have been known since the discovery of superconductivity in 1911 by Kamerlingh-Onnes.

10. Prior to 1986 a person having a bachelor's degree in an engineering discipline, applied science, chemistry, physics or a related discipline could have been trained within one year to reliably test a material for the presence of superconductivity and to flow a superconductive current in a superconductive composition.

11. Prior to 1986 a person of ordinary skill in the art of fabricating a composition according to the teaching of the Bednorz-Mueller application would have: a) a Ph.D. degree in solid state chemistry, applied physics, material science, metallurgy, physics or a related discipline and have done thesis research including work in the fabrication of ceramic materials; or b) have a Ph.D. degree in these same fields having done experimental thesis research plus one to two years post Ph.D. work in the fabrication of ceramic materials; or c) have a master's degree in these same fields and have had five years of materials experience at least some of which is in the fabrication of ceramic materials. Such a person is referred to herein as a person of ordinary skill in the ceramic fabrication art.

12. The general principles of ceramic science referred to by Bednorz and Mueller in their patent application and known to a person of ordinary skill in the ceramic fabrication art can be found in many books and articles published before their discovery, priority date (date of filing of their European Patent Office patent application EPO 0275343A1, January 23, 1987) and initial US Application filing date (May 22, 1987). An exemplary list of books describing the general principles of ceramic fabrication are:

- a) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is in Attachment B.
- b) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is in Attachment C.

- c) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is in Attachment D.
- d) Structure, Properties and Preparation of Perovskite-Type Compounds, F. S. Galasso , Pergamon Press, 1969, in particular pages 159-186, a copy of which is in Attachment E.

These references were previously submitted with the Affidavit of Thomas Shaw submitted December 15, 1998.

13. An exemplary list of articles applying the general principles of ceramic fabrication to the types of materials described in Applicants' specification are:

- a) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+\epsilon}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981). See Attachment F.
- b) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic (This is referred to in the Bednorz-Mueller application at page 21, lines 1-2) Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985. See Attachment G.
- c) Oxygen Intercalation in Mixed Valence Copper Oxides Related to the Perovskite, C. Michel et al., Revue de Chemie Minerale, 21, p. 407, 1984. (This is referred to in the Bednorz-Mueller application at page 27, lines 1-2). See Attachment H.
- d) Thermal Behaviour of Compositions in the Systems  $x BaTiO_3 + (1-x) Ba(Ln_{0.5} B_{0.5}) O_3$ , V.S. Chincholkar et al., Therm. Anal. 6th, Vol. 2., p. 251-6, 1980. See Attachment I.

14. The Bednorz-Mueller application in the paragraph bridging pages 6 and 7 states in regard to the high  $T_c$  materials:

These compositions can carry supercurrents (i.e., electrical currents in a substantially zero resistance state of the composition) at temperatures greater than 26°K. In general, the compositions are characterized as mixed transition metal oxide systems where the transition metal oxide can exhibit multivalent behavior. These compositions have a layer-type crystalline structure, often perovskite-like, and can contain a rare earth or rare earth-like element. A rare earth-like element (sometimes termed a near rare earth element is one whose properties make it essentially a rare earth element. An example is a group IIIB element of the periodic table, such as La. Substitutions can be found in the rare earth (or rare earth-like) site or in the transition metal sites of the compositions. For example, the rare earth site can also include alkaline earth elements selected from group IIA of the periodic table, or a combination of rare earth or rare earth-like elements and alkaline earth elements. Examples of suitable alkaline earths include Ca, Sr, and Ba. The transition metal site can include a transition metal exhibiting mixed valent behavior, and can include more than one transition metal. A particularly good example of a suitable transition metal is copper. As will be apparent later, Cu-oxide based systems provide unique and excellent properties as high  $T_c$  superconductors. An example of a superconductive composition having high  $T_c$  is the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen. Examples of transition metal elements include Cu, Ni, Cr etc. In particular, transition metals that can exhibit multi-valent states are very suitable. The rare earth elements are typically elements 58-71 of the periodic table, including Ce, Nd, etc.

15. In the passage quoted in paragraph 14 the general formula is RE-TM-O "where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen." This paragraph states "Substitutions can be found in the rare earth (or rare earth-like) site or in the transition metal sites of the compositions. For example, the rare earth site can also include alkaline earth elements selected from group IIA of the periodic table, or a combination of rare earth or rare earth-like elements and alkaline earth elements." Thus applicants teach that RE can be something other than an rare earth. For example, it can be an alkaline earth, but is not limited to a alkaline earth element. It can be an element that has the same effect as an alkaline earth or rare-earth element, that is a rare earth like element. Also, this passage teaches that TM can be substituted with another element, for example, but not limited to, a rare earth, alkaline earth or some other element that acts in place of the transition metal.

16. The following table is compiled from the Table 1 of the Article by Rao (See Attachment AB) and the Table of high T<sub>c</sub> materials from the "CRC Handbook of Chemistry and Physics" 2000-2001 Edition (See Attachment AC). An asterisk in column 5 indicated that the composition of column 2 does not come within the scope of the claims allowed in the Office Action of July 28, 2004.

17. I have reviewed the Office Action dated July 28, 2004, which states at page 6 "The present specification is deemed to be enabled only for compositions comprising a transition metal oxide containing at least a) an alkaline earth element and b) a rare-earth element of Group IIIB element." I disagree for the reasons given herein.

18. Composite Table

1 #	2 MATERIAL	3 RAO ARTICLE	4 HANDBOOK OF CHEM & PHYSICS	5	6 ALKALINE EARTH ELEMENT	7 RARE EARTH ELEMEN NT
1	La <sub>2</sub> CuO <sub>4+δ</sub>	✓	✓	*	N	Y
2	La <sub>2-x</sub> Sr <sub>x</sub> (Ba <sub>x</sub> )CuO <sub>4</sub>	✓	✓		Y	Y
3	La <sub>2</sub> Ca <sub>1-x</sub> Sr <sub>x</sub> Cu <sub>2</sub> O <sub>6</sub>	✓	✓		Y	Y

4	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	✓	✓		Y	Y
5	YBa <sub>2</sub> Cu <sub>4</sub> O <sub>8</sub>	✓	✓		Y	Y
6	Y <sub>2</sub> Ba <sub>4</sub> Cu <sub>7</sub> O <sub>15</sub>	✓	✓		Y	Y
7	Bi <sub>2</sub> Sr <sub>2</sub> CuO <sub>6</sub>	✓	✓	*	Y	N
8	Bi <sub>2</sub> Ca <sub>2</sub> Sr <sub>2</sub> Cu <sub>2</sub> O <sub>8</sub>	✓	✓	*	Y	N
9	Bi <sub>2</sub> Ca <sub>2</sub> Sr <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	✓	✓	*	Y	N
10	Bi <sub>2</sub> Sr <sub>2</sub> (Ln <sub>1-x</sub> Ce <sub>x</sub> ) <sub>2</sub> Cu <sub>2</sub> O <sub>10</sub>	✓	✓		Y	Y
11	Tl <sub>2</sub> Ba <sub>2</sub> CuO <sub>6</sub>	✓	✓	*	Y	N
12	Tl <sub>2</sub> CaBa <sub>2</sub> Cu <sub>2</sub> O <sub>8</sub>	✓	✓	*	Y	N
13	Tl <sub>2</sub> Ca <sub>2</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	✓	✓	*	Y	N
14	Tl(BaLa)CuO <sub>5</sub>	✓	✓		Y	Y
15	Tl(SrLa)CuO <sub>5</sub>	✓	✓		Y	Y
16	(Tl <sub>0.5</sub> Pb <sub>0.5</sub> )Sr <sub>2</sub> CuO <sub>5</sub>	✓	✓	*	Y	N
17	TlCaBa <sub>2</sub> Cu <sub>2</sub> O <sub>7</sub>	✓	✓	*	Y	N
18	(Tl <sub>0.5</sub> Pb <sub>0.5</sub> )CaSr <sub>2</sub> Cu <sub>2</sub> O <sub>7</sub>	✓	✓	*	Y	N
19	TlSr <sub>2</sub> Y <sub>0.5</sub> Ca <sub>0.5</sub> Cu <sub>2</sub> O <sub>7</sub>	✓	✓		Y	Y
20	TlCa <sub>2</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>8</sub>	✓	✓	*	Y	N
21	(Tl <sub>0.5</sub> Pb <sub>0.5</sub> )Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>9</sub>	✓	✓	*	Y	N
22	TlBa <sub>2</sub> (Ln <sub>1-x</sub> Ce <sub>x</sub> ) <sub>2</sub> Cu <sub>2</sub> O <sub>9</sub>	✓	✓		Y	Y
23	Pb <sub>2</sub> Sr <sub>2</sub> Ln <sub>0.5</sub> Ca <sub>0.5</sub> Cu <sub>3</sub> O <sub>8</sub>	✓	✓		Y	Y
24	Pb <sub>2</sub> (Sr,La) <sub>2</sub> Cu <sub>2</sub> O <sub>6</sub>	✓	✓		Y	Y
25	(Pb,Cu)Sr <sub>2</sub> (Ln,Ca)Cu <sub>2</sub> O <sub>7</sub>	✓	✓		Y	Y
26	(Pb,Cu)(Sr,Eu)(Eu,Ce)Cu <sub>2</sub> O <sub>x</sub>	✓	✓		Y	Y
27	Nd <sub>2-x</sub> Ce <sub>x</sub> CuO <sub>4</sub>	✓	✓	*	N	Y
28	Ca <sub>1-x</sub> Nd <sub>x</sub> CuO <sub>2</sub>	✓			Y	Y
29	Sr <sub>1-x</sub> Nd <sub>x</sub> CuO <sub>2</sub>	✓	✓		Y	Y
30	Ca <sub>1-x</sub> Sr <sub>x</sub> CuO <sub>2</sub>		✓	*	Y	N
31	Ba <sub>0.6</sub> K <sub>0.4</sub> BiO <sub>3</sub>		✓	*	Y	N
32	Rb <sub>2</sub> C <sub>5</sub> C <sub>60</sub>		✓	*	N	Y
33	NdBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>		✓		Y	Y
34	SmBaSrCuO <sub>7</sub>		✓		Y	Y
35	EuBaSrCu <sub>3</sub> O <sub>7</sub>		✓		Y	Y
36	BaSrCu <sub>3</sub> O <sub>7</sub>		✓	*	Y	N
37	DyBaSrCu <sub>3</sub> O <sub>7</sub>		✓		Y	Y
38	HuBaSrCu <sub>3</sub> O <sub>7</sub>		✓		Y	Y
39	ErBaSrCu <sub>3</sub> O <sub>7</sub> (Multiphase)		✓		Y	Y
40	TmBaSrCu <sub>3</sub> O <sub>7</sub> (Multiphase)		✓		Y	Y

41	YBaSrCu <sub>3</sub> O <sub>7</sub>		✓	*	Y	Y
42	HgBa <sub>2</sub> CuO <sub>2</sub>		✓	*	Y	N
43	HgBa <sub>2</sub> CaCu <sub>2</sub> O <sub>6</sub> (annealed in O <sub>2</sub> )		✓	*	Y	N
44	HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8</sub>		✓	*	Y	N
45	HgBa <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>10</sub>		✓	*	Y	N

19. The first composition, La<sub>2</sub>CuO<sub>4+δ</sub>, has the form RE<sub>2</sub>CuO<sub>4</sub> which is explicitly taught by Bednorz and Mueller. The δ indicates that there is a nonstoichiometric amount of oxygen.

20. The Bednorz-Mueller application teaches at page 11, line 19 to page 12, line 7:

An example of a superconductive compound having a layer-type structure in accordance with the present invention is an oxide of the general composition RE<sub>2</sub>TMO<sub>4</sub> where RE stands for the rare earths (lanthanides) or rare earth-like elements and TM stands for a transition metal. In these compounds the RE portion can be partially substituted by one or more members of the alkaline earth group of elements. In these particular compounds, the oxygen content is at a deficit. For example, one such compound that meets this general description is lanthanum copper oxide La<sub>2</sub>CuO<sub>4</sub>...

21. The Bednorz-Mueller application at page 15, last paragraph states "Despite their metallic character, the Ba-La-Cu-O type materials are essentially ceramics, as are other compounds of the RE<sub>2</sub>TMO<sub>4</sub> type, and their manufacture generally follows known principles of ceramic fabrication."

22. Compound number 27 of the composite table contains Nd and Ce, both rare earth elements. All of the other compounds of the composite table, except for number 32, have O and one of the alkaline earth elements which as stated above is explicitly taught by applicants. Compound 31 is a BiO<sub>3</sub> compound in which TM is substituted by another element, here Bi, as explicitly taught by Applicants in the paragraph quoted above.

23. The rare earth elements are Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. See the Handbook of Chemistry and Physics 59th edition 1978-1979 page B262 in Appendix A. The transition elements are identified in the periodic table from the inside front cover of the Handbook of Chemistry and Physics in Appendix A.

24. The basic theory of superconductivity has been known many years before Applicants' discovery. For example, see the book "Theory of Superconductivity", M. von Laue, Academic Press, Inc., 1952 (See Attachment AD).

25. In the composite table, compound numbers 7 to 10 and 31 are Bismuth (Bi) compounds. Compound number 12 to 22 are Thallium (Tl) compounds. Compound numbers 23 to 26 are lead (Pb) compounds. Compounds 42 to 45 are Mercury (Hg) compounds. Those compounds that do not come within the scope of an allowed claims (the compounds which are not marked with an asterisk in column 3 of the composite table) are primarily the Bi, Tl, Pb and Hg compounds. These compounds are made according to the principles of ceramic science known prior to applicant's filing date. For example, Attachments J, K, L, and M contain the following articles:

Attachment J - Phys. Rev. B. Vol. 38, No. 16, p. 6531 (1988) is directed to Thallium compounds.

Attachment K - Jap. Joun. of Appl. Phys., Vol. 27, No. 2, p. L209-L210 (1988) is directed to Bismuth (Bi) compounds.

Attachment L - Letter to Nature, Vol. 38, No. 2, p. 226 (18 March 1993) is directed to Mercury (Hg) compounds.

Attachment M - Nature, Vol. 336, p. 211 (17 November 1988) is directed to Lead (Pb) based compounds.

26. The article of Attachment J (directed to Tl compounds) states at page 6531, left column:

The samples were prepared by thoroughly mixing suitable amounts of  $Tl_2O_3$ ,  $CaO$ ,  $BaO_2$ , and  $CuO$ , and forming a pellet of this mixture under pressure. The pellet was then wrapped in gold foil, sealed in quartz tube containing slightly less than 1 atm of oxygen, and baked for approximately 3 h at  $\approx 880^{\circ}C$ .

This is according to the general principles of ceramic science known prior to applicant's priority date.

27. The article of Attachment K (directed to Bi compounds) states at page L209:

The Bi-Sr-Ca-Cu-O oxide samples were prepared from powder reagents of  $Bi_2O_3$ ,  $SrCO_3$ ,  $CaCO_3$  and  $CuO$ . The appropriate amounts of powders were mixed, calcined at  $800-870^{\circ}C$  for 5 h, thoroughly reground and then cold-pressed into disk-shape pellets (20 mm in diameter and 2 mm in thickness) at a pressure of 2 ton.cm<sup>2</sup>. Most of the pellets were sintered at about  $870^{\circ}C$  in air or in an oxygen atmosphere and then furnace-cooled to room temperature.

This is according to the general principles of ceramic science known prior to applicant's priority date.

28. The article of Attachment L (directed to Hg compounds) states at page 226:

The samples were prepared by solid state reaction between stoichiometric mixtures of  $\text{Ba}_2\text{CuO}_{3+\delta}$  and yellow  $\text{HgO}$  (98% purity, Aldrich). The precursor  $\text{Ba}_2\text{CuO}_{3+\delta}$  was obtained by the same type of reaction between  $\text{BaO}_2$  (95% purity, Aldrich) and  $\text{CuO}$  (NormalPur, Prolabo) at 930°C in oxygen, according to the procedure described by De Leeuw et al.<sup>6</sup>. The powders were ground in an agate mortar and placed in silica tubes. All these operations were carried out in a dry box. After evacuation, the tubes were sealed, placed in steel containers, as described in ref. 3, and heated for 5 h to reach ~800°C. The samples were then cooled in the furnace, reaching room temperature after ~10 h.

This is according to the general principles of ceramic science known prior to applicant's priority date.

29. The article of Attachment M (directed to Pb compounds) states at page 211, left column:

The preparative conditions for the new materials are considerably more stringent than for the previously known copper-based superconductors. Direct synthesis of members of this family by reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 900°C is not possible because of the stability of the oxidized  $\text{SrPbO}_3$ -based perovskite. Successful synthesis is accomplished by the reaction of  $\text{PbO}$  with pre-reacted ( $\text{Sr}$ ,  $\text{Ca}$ ,  $\text{Ln}$ ) oxide precursors. The precursors are prepared from oxides and carbonates in the appropriate metal ratios, calcined for 16 hours (in dense  $\text{Al}_2\text{O}_3$  crucibles) at 920-980°C in air with one intermediate grinding.

This is according to the principles of ceramic science known prior to applicant's priority date.

30. A person of ordinary skill in the art of the fabrication of ceramic materials would be motivated by the teaching of the Bednorz-Mueller application to investigate compositions for high superconductivity other than the compositions specifically fabricated by Bednorz and Mueller.

31. In Attachment U, there is a list of perovskite materials from pages 191 to 207 in the book "Structure, Properties and Preparation of Perovskite-Type Compounds" by F. S. Galasso, published in 1969, which is Attachment E hereto. This list contains about 300 compounds. Thus, what the term "Perovskite-type" means and how to make these compounds was well known to a person of ordinary skill in the art in 1969, more than 17 years before the Applicants' priority date (January 23, 1987).

This is clear evidence that a person of skill in the art of fabrication of ceramic materials knows (prior to Applicants' priority date) how to make the types of materials in Table 1 of the Rao Article and the Table from the Handbook of Chemistry and Physics as listed in the composite table above in paragraph 17.

32. The standard reference "Landolt-Börnstein", Volumn 4, "Magnetic and Other Properties of Oxides and Related Compounds Part A" (1970) lists at page 148 to 206 Perovskite and Perovskite-related structures. (See Attachment N). Section 3.2 starting at page 190 is entitled "Descriptions of perovskite-related structures". The German title is "Perowskit-ähnliche Strukturen". The German word "ähnliche" can be translated in English as "like". The Langenscheidt's German-English, English-German Dictionary 1970, at page 446 translates the English "like" as the German "ähnliche". (See Attachment O). Pages 126 to 147 of Attachment N describes "crystallographic and magnetic properties of perovskite and perovskite-related compounds", see title of Section 3 at page 126. Section 3.2.3.1 starting at page 192 of "Landolt-Börnstein" Vol. 4 (See Attachment N) is entitled "Bismuth Compounds". Thus Bismuth

perovskite-like compounds and how to make them were well known more than 16 years prior to Applicants' priority date. Thus the "Landolt Börnstein" book published in 1970, more than 16 years before Applicants' priority date (January 23, 1987), shows that the term "perovskite-like" or "perovskite related" is understood by persons of skill in the art prior to Applicants' priority date. Moreover, the "Landolt-Börnstein" book cites references for each compound listed. Thus a person of ordinary skill in the art of ceramic fabrication knows how to make each of these compounds. Pages 376-380 of Attachment N has figures showing the crystal structure of compounds containing Bi and Pb.

33. The standard reference "Landolt-Börnstein, Volume 3, Ferro- and Antiferroelectric Substances" (1969) provides at pages 571-584 an index to substances. (See Attachment P). This list contains numerous Bi and Pb containing compounds. See, for example pages 578 and 582-584. Thus a person of ordinary skill in the art of ceramic fabrication would be motivated by Applicants' application to fabricate Bi and/or Pb containing compounds that come within the scope of the Applicants' claims.

34. The standard reference "Landolt-Börnstein Volume 3 Ferro- and Antiferroelectric Substances" (1969) (See Attachment P) at page 37, section 1 is entitled "Perovskite-type oxides." This standard reference was published more than 17 years before Applicants' priority date (January 23, 1987). The properties of perovskite-type oxides are listed from pages 37 to 88. Thus the term perovskite-type was well known and understood by persons of skill in the art of ceramic fabrication prior to Applicants' priority date and more than 17 years before Applicants' priority date persons of ordinary skill in the art knew how to make Bi, Pb and many other perovskite, perovskite-like, perovskite-related and perovskite-type compounds.

35. At page 14, line 10-15 of the Bednorz-Mueller application, Applicants' state "samples in the Ba-La-Cu-O system, when subjected to x-ray analysis, revealed three individual crystallographic phases V.12. a first layer-type perovskite-like phase, related to the  $K_2NiF_4$  structure ..." Applicants' priority document EP0275343A1 filed July 27, 1988, is entitled "New Superconductive Compounds of the  $K_2NiF_4$  Structural Type Having a High Transition Temperature, and Method for Fabricating Same." See (See Attachment AE). The book "Structure and Properties of Inorganic Solids" by Francis S. Galasso, Pergamon Press (1969) at page 190 lists examples of Tantillium (Tl) compounds in the  $K_2NiF_4$  structure. (See Attachment Q). Thus based on Applicants' teachings prior to Applicants' priority date, a person of ordinary skill in the art of ceramic fabrication would be motivated to fabricate Thallium based compounds to test for high  $T_c$  superconductivity.

36. The book "Crystal Structures" Volume 4, by Ralph W. G. Wyckoff, Interscience Publishers, 1960 states at page 96 "This structure, like these of  $Bi_2Ti_2O_{12}$  (IX,  $F_{12}$ ) and  $Ba_2Bi_4Ti_4O_9$  (XI, 13) is built up of alternating  $Bi_2O_2$  and perovskite-like layers." Thus layer of perovskite-like Bismuth compounds was well known in the art in 1960 more than 26 years before Applicants' priority date. (See Attachment R).

37. The book "Modern Oxide Materials Preparation, Properties and Device Applications" edited by Cockayne and Jones, Academic Press (1972) states (See Attachment S) at page 155 under the heading "Layer Structure Oxides and Complex Compounds":

"A large number of layer structure compounds of general formula  $(Bi_2O_2)^{2+}(A_{x-1}B_xO_{3x+1})^{2-}$  have been reported (Smolenskii et al. 1961; Subbarao, 1962), where A = Ca, Sr, Ba, Pb, etc., B = Ti, Nb, Ta and x = 2, 3, 4, or 5. The structure had been previously investigated by Aurivillius (1949) who described them in terms of Alternate  $(Bi_2O_2)^{2+}$  layers and perovskite layers of oxygen octahedra. Few have been found to be ferroelectric and include  $SrBi_2Ta_2O_9$  ( $T_c = 583^\circ K$ ),  $PbBi_2Ta_2O_9$  ( $T_c = 703^\circ K$ ),  $BiBi_3Ti_2TiO_{12}$  or

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$  ( $T_c = 948^\circ\text{K}$ ),  $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  ( $T_c = 598^\circ\text{K}$ ) and  $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  ( $T_c = 583^\circ\text{K}$ ). Only bismuth titanate  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  has been investigated in detail in the single crystal form and is finding applications in optical stores (Cummins, 1967) because of its unique ferroelectric-optical switching properties. The ceramics of other members have some interest because of their dielectric properties. More complex compounds and solid solutions are realizable in these layer structure oxides but none have significant practical application."

Thus the term layered oxides was well known and understood prior to Applicants' priority date. Moreover, layered Bi and Pb compounds were well known in 1972 more than 15 years before Applicants' priority date.

38. The standard reference "Landolt-Börnstein, Volume 3, Ferro and Antiferroelectric Substances" (1969) at pages 107 to 114 (See Attachment T) list "layer-structure oxides" and their properties. Thus the term "layered compounds" was well known in the art of ceramic fabrication in 1969 more than 16 years prior to Applicants' priority date and how to make layered compounds was well known prior to applicants priority date.

39. Layer perovskite type Bi and Pb compounds closely related to the Bi and Pb high  $T_c$  compounds in the composite table above in paragraph 17 have been known for some time. For example, the following is a list of four articles which were published about 35 years prior to Applicants' first publication date:

- (1) Attachment V - "Mixed bismuth oxides with layer lattices", B. Aurivillius, Arkiv Kemi 1, 463, (1950).
- (2) Attachment W - "Mixed bismuth oxides with layered lattices ", B. Aurivillius, Arkiv Kemi 1, 499, (1950).

(3) Attachment X - "Mixed bismuth oxides with layered lattices ", B. Aurivillius, Arkiv Kemi 2, 519, (1951).

(4) Attachment Y - "The structure of  $\text{Bi}_2\text{NbO}_5\text{F}$  and isomorphous compounds", B. Aurivillius, Arkiv Kemi 5, 39, (1952).

These articles will be referred to as Aurivillius 1, 2, 3 and 4, respectively.

40. Attachment V (Aurivillius 1), at page 463, the first page, has the subtitle "I. The structure type of  $\text{CaNb}_2\text{Bi}_2\text{O}_9$ . Attachment V states at page 463:

X-ray analysis ... seemed to show that the structure was built up of  $\text{Bi}_2\text{O}_2^{2+}$  layers parallel to the basal plane and sheets of composition  $\text{Bi}_2\text{Ti}_3\text{O}^{2-}_{10}$ . The atomic arrangement within the  $\text{Bi}_2\text{Ti}_3\text{O}^{2-}_{10}$  sheets seemed to be the same as in structure of the perovskite type and the structure could then be described as consisting of  $\text{Bi}_2\text{O}_2^{2+}$  layers between which double perovskite layers are inserted.

41. Attachment V (Aurivillius 1) at page 464 has a section entitled " $\text{PbBi}_2\text{Nb}_2\text{O}_9$  Phase". And at page 471 has a section entitled " $\text{Bi}_3\text{NbTiO}_9$ ". And at page 475 has a table of compounds having the " $\text{CaBi}_2\text{Nb}_2\text{O}_9$  structure" listing the following compounds  $\text{Bi}_3\text{NbTiO}_9$ ,  $\text{Bi}_3\text{TaTiO}_9$ ,  $\text{CaBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{SrBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ,  $\text{BaBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{PbBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{NaBi}_5\text{Nb}_4\text{O}_{18}$ ,  $\text{KBi}_5\text{Nb}_4\text{O}_{18}$ . Thus Bi and Pb layered perovskite compounds were well known in the art about 35 years prior to Applicants' priority date.

42. Attachment W (Aurivillius 2) at page 499, the first page, has the subtitle "II Structure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ". And at page 510, Fig. 4 shows a crystal structure in which "A" denotes a perovskite layer  $\text{Bi}_2\text{Ti}_3\text{O}^{2-}_{10}$ , C  $\text{Bi}_2\text{O}_2^{2+}$  layers and B unit cells of the hypothetical perovskite structure  $\text{BiTiO}_3$ .

43. Attachment X (Aurivillius 3) has at page 519, the first page, the subtitle "III Structure of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ". And in the first paragraph on page 519 states referring to the articles of Attachments V (Aurivillius 1), and W (Aurivillius 2) "X ray studies on the compounds  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  [the article of Attachment V] and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  [the article of Attachment W] have shown that the comparatively complicated chemical formulae of these compounds can be explained by simple layer structures being built up from  $\text{Bi}_2\text{O}_2^+$  layers and perovskite layers. The unit cells are pictured schematically in Figs. 1a and 1c." And Fig. 4 at page 526 shows "One half of a unit cell of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ . A denotes the perovskite region and B the  $\text{Me}_2\text{O}_4$  layer" where Me represents a metal atom.

44. Attachment Y (Aurivillius 4) is direct to structures having the  $\text{Bi}_3\text{N}_{10}\text{O}_3\text{F}$  structure.

45. Attachment AA is a list of Hg containing solid state compounds from the 1989 Powder Diffraction File Index. Applicants do not have available to them an index from prior to Applicants' priority date. The Powder Diffraction File list is a compilation of all known solid state compounds with reference to articles directed to the properties of these compositions and the methods of fabrication. From Attachment AA it can be seen, for example, that there are numerous examples of Hg based compounds. Similarly, there are examples of other compounds in the Powder Diffraction File. A person of ordinary skill in the art is aware of the Powder Diffraction File and can from this file find a reference providing details on how to fabricate these compounds. Thus persons of ordinary skill in the art would be motivated by Applicants' teaching to look to the Powder Diffraction File for examples of previously fabricated composition expected to have properties similar to those described in Applicants' teaching.

46. It is generally recognized that it is not difficult to fabricate transition metal oxides and in particular copper metal oxides that are superconductive after the discovery by Applicants of composition, such as transition metal oxides, that are high T<sub>c</sub> superconductors. This is noted in the book "Copper Oxide Superconductors" by Charles P. Poole, Jr., Timir Datta and Horacio A. Farach, John Wiley & Sons (1998),

referred to herein as Poole 1988: Chapter 5 of Poole 1988 (See Attachment AF) in the book entitled "Preparation and Characterization of Samples" states at page 59 "[c]opper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials". Poole 1988 further states at page 61 "[i]n this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatlfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor." Poole 1988 further states at pages 61-62 "[i]n the solid state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates or carbonates of Ba, Bi, La, Sr, Ti, Y or other elements. ... These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcination for an extended period (~20hr) at elevated temperatures (~900°C). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step." This is generally the same as the specific examples provided by Applicants and as generally described at pages 8, line 19, to page 9, line 5, of the Bednorz-Mueller application which states "[t]he methods by which these superconductive compositions can be made can use known principals of ceramic fabrication, including the mixing of powders containing the rare earth or rare earth-like, alkaline earth, and transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air. A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal." Consequently, it is my opinion that Applicants have fully enabled high T<sub>c</sub> materials oxides and their claims.

47. Charles Poole et al. published another book in 1995 entitled "Superconductivity" Academic Press which has a Chapter 7 on "Perovskite and Cuprate Crystallographic Structures". (See Attachment Z). This book will be referred to as Poole 1995.

At page 179 of Poole 1995 states:

#### V. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Müller (1986) referred to their samples as "metallic, oxygen-deficient ... perovskite-like mixed-valence copper compounds." Subsequent work has confirmed that the new superconductors do indeed possess these characteristics.

I agree with this statement.

48. The book "The New Superconductors", by Frank J. Owens and Charles P. Poole, Plenum Press, 1996, referred to herein as Poole 1996 in Chapter 8 entitled "New High Temperature Superconductors" starting a page 97 (See Attachment AG) shows in Section 8.3 starting at page 98 entitled "Layered Structure of the Cuprates" schematic diagrams of the layered structure of the cuprate superconductors. Poole 1996 states in the first sentence of Section 8.3 at page 98 "All cuprate superconductors have the layered structure shown in Fig. 8.1." This is consistent with the teaching of Bednorz and Mueller that "These compositions have a layer-type Crystalline Structure often Perovskite-like" as noted in paragraph 14 above. Poole 1996 further states in the first sentence of Section 8.3 at page 98 "The flow of supercurrent takes place in conduction layers and bonding layers support and hold together the conduction layers". The caption of Fig. 8.1 states "Layering scheme of the cuprate superconductors". Fig. 8.3 shows details of the conduction layers for difference sequence of copper oxide planes and Fig. 8.4 presents details of the bonding layers for several of the cuprates which include binding layers for lanthanum superconductor  $\text{La}_2\text{CuO}_4$ , neodymium superconductor  $\text{Nd}_2\text{CuO}_4$ , yttrium superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{2n+4}$ , bismuth

superconductor  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , thallium superconductor  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , and mercury superconductor  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ . Fig. 8.5 at pages 102 and 103 show a schematic atomic structure showing the layering scheme for thallium superconductors. Fig. 8.10 at page 109 shows a schematic crystal structure showing the layering scheme for  $\text{La}_2\text{CuO}_4$ . Fig. 8.11 at page 110 shows a schematic crystal structure showing the layering scheme for  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{6+\delta}$ . The layering shown in Poole 1996 for high  $T_c$  superconductors is consistent with the layering as taught by Bednorz and Mueller in their patent application.

49. Thus Poole 1988 states that the high  $T_c$  superconducting materials "are not difficult to synthesize" and Poole 1995 states that "the new superconductors do indeed possess [the] characteristics" that Applicants' specification describes these new superconductors to have. Poole 1996 provide details showing that high  $T_c$  superconductors are layered or layer-like as taught by Bednorz and Mueller. Therefore, as of Applicants' priority date persons of ordinary skill in the art of ceramic fabrication were enabled to practice Applicants' invention to the full scope that it is presently claimed, including in the claims that are not allowed from the teaching in the Bednorz-Mueller application without undue experimentation that is by following the teaching of Bednorz and Mueller in combination with what was known to persons of ordinary skill in the art of ceramic fabrication. The experiments to make high  $T_c$  superconductors not specifically identified in the Bednorz-Mueller application were made by principles of ceramic fabrication prior to the date of their first publication. It is within the skill of a person of ordinary skill in the art of ceramic fabrication to make compositions according to the teaching of the Bednorz-Mueller application to determine whether or not they are high  $T_c$  superconductors without undue experimentation.

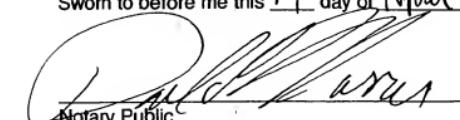
50. I have personally made many samples of high Tc superconductors following the teaching of Bednorz and Mueller as found in their patent applications. In making these materials it was not necessary to use starting materials in stoichiometric proportions to produce a high T<sub>c</sub> superconductor with insignificant secondary phases or multi-phase compositions, having a superconducting portion and a non-superconducting portion, where the composite was a high T<sub>c</sub> superconductor. Consequently, following the teaching of Bednorz and Mueller and principles of ceramic science known prior to their discovery, I made, and persons of skill in the ceramic arts were able to make, high T<sub>c</sub> superconductors without exerting extreme care in preparing the composition. Thus I made and persons of skill in the ceramic arts were able to make high T<sub>c</sub> superconductors following the teaching of Bednorz and Mueller, without experimentation beyond what was well known to a person of ordinary skill in the ceramic arts prior to the discovery by Bednorz and Mueller.

51. I hereby swear that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or patent issued thereon.

Date: 14th April 2005

By: Thomas M. Shaw  
Thomas M. Shaw

Sworn to before me this 14 day of April, 2005.

  
Notary Public

DANIEL P. MORRIS  
NOTARY PUBLIC, State of New York  
No. 4888676  
Qualified in Westchester County  
Commission Expires March 16, 192007

**ATTACHMENT 1**

Thomas M. Shaw

IBM Thomas J. Watson Research Center  
P.O. Box 218  
Yorktown Heights, NY 10598  
Phone: (914) 945-3196

**Education:**

1981 Ph.D.	Materials Science - University of California at Berkeley
1978 Masters of Science	Materials Science - University of California at Berkeley
1975 Bachelors of Science	Engineering in Metallurgy and Materials Science - University of Liverpool

**Work Experience:**

1994-Present Research Staff Member at IBM Thomas J. Watson Research Center working in Materials Science  
1984-1994 Research Staff Member at IBM Thomas J. Watson Research Center working in Ceramics Science  
1982-1984 Member of the technical staff at Rockwell International Science Center working in Ceramics Science  
1981-1982 Postdoctoral Associate at Cornell University working in Ceramics Science

**Professional Positions:**

A fellow of the American Ceramics Society

**Honors:**

1981 John E. Dorn Award for thesis.

**Publications:**

Has authored or co-authored more than 150 publications and 21 patents.

His research interests include, ferroelectric thin films, processing and microstructure control of ceramic materials, microscopy of materials, interfacial energy driven processes, liquid phase sintering, porous materials, diffusion in thin films, electrical and mechanical properties materials and the reliability of interconnect structures.

\*\* TX STATUS REPORT \*\*

AS OF APR 14 '05 15:06 PAGE.01

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**BRIEF ATTACHMENT AN**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: April 5, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated July 28, 2004, please consider the  
following:

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

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Applicants: Bednorz et al.

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TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

AFFIDAVIT UNDER 37 C.F.R. 1.132

Sir:

I, Chang C. Tsuei, being duly sworn, do hereby depose and state:

1. I received a B. S. degree in Mechanical Engineering from National Taiwan University (1960), and M. S. and Ph.D. degrees in Material Science (1963, 1966) respectively from California Institute of Technology.
2. I refer to Attachments A to Z and AA herein which were submitted in a separate paper designated as "FIRST SUPPLEMENTAL AMENDMENT" in response to the Office Action dated July 28, 2004. I also refer to Attachments AB to AG which were submitted in a separate paper designated as "THIRD SUPPLEMENTAL AMENDMENT" in response to the Office Action dated July 28, 2004.
3. I have worked as a research staff member and manager in the physics of superconducting, amorphous and structured materials at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1973 to the present.
4. I have worked in the fabrication of and characterization of high temperature superconductor and related materials from 1973 to the present.

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3. I have worked as a research staff member and manager in the physics of superconducting, amorphous and structured materials at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1973 to the present.
4. I have worked in the fabrication of and characterization of high temperature superconductor and related materials from 1973 to the present.

5. My resume and list of publications is in Attachment 1 included with this affidavit.
6. This affidavit is in addition to my affidavit dated December 15, 1998. I have reviewed the above-identified patent application (Bednorz-Mueller application) and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity in a material having a  $T_c \geq 26^{\circ}\text{K}$  and that subsequent developments in this field have been based on this work.
7. All the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner, have similar magnetic properties, and have similar structural properties.
8. Once a person of skill in the art knows of a specific type of composition described in the Bednorz-Mueller application which is superconducting at greater than or equal to  $26^{\circ}\text{K}$ , such a person of skill in the art, using the techniques described in the Bednorz-Mueller application, which includes all principles of ceramic fabrication known at the time the application was initially filed, can make the compositions encompassed by the claims of the Bednorz-Mueller application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art of the fabrication of ceramic materials. This is why the work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period after their discovery. Bednorz and Mueller's discovery was first reported in Z. Phys. B 64 page 189-193 (1996).
9. The techniques for placing a superconductive composition into a superconducting state have been known since the discovery of superconductivity in 1911 by Kamerlingh-Onnes.

10. Prior to 1986 a person having a bachelor's degree in an engineering discipline, applied science, chemistry, physics or a related discipline could have been trained within one year to reliably test a material for the presence of superconductivity and to flow a superconductive current in a superconductive composition.

11. Prior to 1986 a person of ordinary skill in the art of fabricating a composition according to the teaching of the Bednorz-Mueller application would have: a) a Ph.D. degree in solid state chemistry, applied physics, material science, metallurgy, physics or a related discipline and have done thesis research including work in the fabrication of ceramic materials; or b) have a Ph.D. degree in these same fields having done experimental thesis research plus one to two years post Ph.D. work in the fabrication of ceramic materials; or c) have a master's degree in these same fields and have had five years of materials experience at least some of which is in the fabrication of ceramic materials. Such a person is referred to herein as a person of ordinary skill in the ceramic fabrication art.

12. The general principles of ceramic science referred to by Bednorz and Mueller in their patent application and known to a person of ordinary skill in the ceramic fabrication art can be found in many books and articles published before their discovery, priority date (date of filing of their European Patent Office patent application EPO 0275343A1, January 23, 1987) and initial US Application filing date (May 22, 1987). An exemplary list of books describing the general principles of ceramic fabrication are:

- a) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is in Attachment B.
- b) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is in Attachment C.

- c) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is in Attachment D.
- d) Structure, Properties and Preparation of Perovskite-Type Compounds, F. S. Galasso , Pergamon Press, 1969, in particular pages 159-186, a copy of which is in Attachment E.

These references were previously submitted with the Affidavit of Thomas Shaw submitted December 15, 1998.

13. An exemplary list of articles applying the general principles of ceramic fabrication to the types of materials described in Applicants' specification are:

- a) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2-\epsilon}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981). See Attachment F.
- b) The Oxygen Defect Perovskite  $BaLa_4Cu_5.O_{13.4}$ , A Metallic (This is referred to in the Bednorz-Mueller application at page 21, lines 1-2) Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985. See Attachment G.
- c) Oxygen Intercalation in Mixed Valence Copper Oxides Related to the Perovskite, C. Michel et al., Revue de Chemie Minerale, 21, p. 407, 1984. (This is referred to in the Bednorz-Mueller application at page 27, lines 1-2). See Attachment H.
- d) Thermal Behaviour of Compositions in the Systems  $x BaTiO_3 + (1-x) Ba(Ln_{0.5} B_{0.5}) O_3$ , V.S. Chincholkar et al., Therm. Anal. 6th, Vol. 2, p. 251-6, 1980. See Attachment I.

14. The Bednorz-Mueller application in the paragraph bridging pages 6 and 7 states in regard to the high T<sub>c</sub> materials:

These compositions can carry supercurrents (i.e., electrical currents in a substantially zero resistance state of the composition) at temperatures greater than 26°K. In general, the compositions are characterized as mixed transition metal oxide systems where the transition metal oxide can exhibit multivalent behavior. These compositions have a layer-type crystalline structure, often perovskite-like, and can contain a rare earth or rare earth-like element. A rare earth-like element (sometimes termed a near rare earth element is one whose properties make it essentially a rare earth element. An example is a group IIIB element of the periodic table, such as La. Substitutions can be found in the rare earth (or rare earth-like) site or in the transition metal sites of the compositions. For example, the rare earth site can also include alkaline earth elements selected from group IIA of the periodic table, or a combination of rare earth or rare earth-like elements and alkaline earth elements. Examples of suitable alkaline earths include Ca, Sr, and Ba. The transition metal site can include a transition metal exhibiting mixed valent behavior, and can include more than one transition metal. A particularly good example of a suitable transition metal is copper. As will be apparent later, Cu-oxide based systems provide unique and excellent properties as high T<sub>c</sub> superconductors. An example of a superconductive composition having high T<sub>c</sub> is the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen. Examples of transition metal elements include Cu, Ni, Cr etc. In particular, transition metals that can exhibit multi-valent states are very suitable. The rare earth elements are typically elements 58-71 of the periodic table, including Ce, Nd, etc.

15. In the passage quoted in paragraph 14 the general formula is RE-TM-O "where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen." This paragraph states "Substitutions can be found in the rare earth (or rare earth-like) site or in the transition metal sites of the compositions. For example, the rare earth site can also include alkaline earth elements selected from group IIA of the periodic table, or a combination of rare earth or rare earth-like elements and alkaline earth elements." Thus applicants teach that RE can be something other than an rare earth. For example, it can be an alkaline earth, but is not limited to a alkaline earth element. It can be an element that has the same effect as an alkaline earth or rare-earth element, that is a rare earth like element. Also, this passage teaches that TM can be substituted with another element, for example, but not limited to, a rare earth, alkaline earth or some other element that acts in place of the transition metal.

16. The following table is compiled from the Table 1 of the Article by Rao (See Attachment AB) and the Table of high T<sub>c</sub> materials from the "CRC Handbook of Chemistry and Physics" 2000-2001 Edition (See Attachment AC). An asterisk in column 5 indicated that the composition of column 2 does not come within the scope of the claims allowed in the Office Action of July 28, 2004.

17. I have reviewed the Office Action dated July 28, 2004, which states at page 6 "The present specification is deemed to be enabled only for compositions comprising a transition metal oxide containing at least a) an alkaline earth element and b) a rare-earth element of Group IIIB element." I disagree for the reasons given herein.

18. Composite Table

1 #	2 MATERIAL	3 RAO ARTICLE	4 HANDBOOK OF CHEM & PHYSICS	5	6 ALKALINE EARTH ELEMENT	7 RARE EARTH ELEMEN T
1	La <sub>2</sub> CuO <sub>4+δ</sub>	√	√	*	N	Y
2	La <sub>2-x</sub> Sr <sub>x</sub> (Ba <sub>x</sub> )CuO <sub>4</sub>	√	√		Y	Y
3	La <sub>2</sub> Ca <sub>1-x</sub> Sr <sub>x</sub> Cu <sub>2</sub> O <sub>6</sub>	√	√		Y	Y

4	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	✓	✓		Y	Y
5	YBa <sub>2</sub> Cu <sub>4</sub> O <sub>8</sub>	✓	✓		Y	Y
6	Y <sub>2</sub> Ba <sub>4</sub> Cu <sub>7</sub> O <sub>15</sub>	✓	✓		Y	Y
7	Bi <sub>2</sub> Sr <sub>2</sub> Cu <sub>6</sub> O <sub>10</sub>	✓	✓	*	Y	N
8	Bi <sub>2</sub> CaSr <sub>2</sub> Cu <sub>2</sub> O <sub>8</sub>	✓	✓	*	Y	N
9	Bi <sub>2</sub> Ca <sub>2</sub> Sr <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	✓	✓	*	Y	N
10	Bi <sub>2</sub> Sr <sub>2</sub> (Ln <sub>1-x</sub> Cex)Cu <sub>2</sub> O <sub>10</sub>	✓	✓		Y	Y
11	Tl <sub>2</sub> Ba <sub>2</sub> Cu <sub>6</sub> O <sub>10</sub>	✓	✓	*	Y	N
12	Tl <sub>2</sub> CaBa <sub>2</sub> Cu <sub>2</sub> O <sub>8</sub>	✓	✓	*	Y	N
13	Tl <sub>2</sub> Ca <sub>2</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	✓	✓	*	Y	N
14	Tl(BaLa)CuO <sub>5</sub>	✓	✓		Y	Y
15	Tl(SrLa)CuO <sub>5</sub>	✓	✓		Y	Y
16	(Tl <sub>0.5</sub> Pb <sub>0.5</sub> )Sr <sub>2</sub> CuO <sub>5</sub>	✓	✓	*	Y	N
17	TlCaBa <sub>2</sub> Cu <sub>2</sub> O <sub>7</sub>	✓	✓	*	Y	N
18	(Tl <sub>0.5</sub> Pb <sub>0.5</sub> )CaSr <sub>2</sub> Cu <sub>2</sub> O <sub>7</sub>	✓	✓	*	Y	N
19	TlSr <sub>2</sub> Y <sub>0.5</sub> Ca <sub>0.5</sub> Cu <sub>2</sub> O <sub>7</sub>	✓	✓		Y	Y
20	TlCa <sub>2</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>8</sub>	✓	✓	*	Y	N
21	(Tl <sub>0.5</sub> Pb <sub>0.5</sub> )Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>9</sub>	✓	✓	*	Y	N
22	TlBa <sub>2</sub> (Ln <sub>1-x</sub> Cex)Cu <sub>2</sub> O <sub>9</sub>	✓	✓		Y	Y
23	Pb <sub>2</sub> Sr <sub>2</sub> Ln <sub>0.5</sub> Ca <sub>0.5</sub> Cu <sub>3</sub> O <sub>8</sub>	✓	✓		Y	Y
24	Pb <sub>2</sub> (Sr,La) <sub>2</sub> Cu <sub>2</sub> O <sub>6</sub>	✓	✓		Y	Y
25	(Pb,Cu)Sr <sub>2</sub> (Ln,Ca)Cu <sub>2</sub> O <sub>7</sub>	✓	✓		Y	Y
26	(Pb,Cu)(Sr,Eu)(Eu,Ce)Cu <sub>2</sub> O <sub>x</sub>	✓	✓		Y	Y
27	Nd <sub>2-x</sub> Ce <sub>x</sub> CuO <sub>4</sub>	✓	✓	*	N	Y
28	Ca <sub>1-x</sub> Nd <sub>x</sub> CuO <sub>2</sub>	✓			Y	Y
29	Sr <sub>1-x</sub> Nd <sub>x</sub> CuO <sub>2</sub>	✓	✓		Y	Y
30	Ca <sub>1-x</sub> Sr <sub>x</sub> CuO <sub>2</sub>		✓	*	Y	N
31	Ba <sub>0.6</sub> K <sub>0.4</sub> BiO <sub>3</sub>		✓	*	Y	N
32	Rb <sub>2</sub> C <sub>5</sub> C <sub>60</sub>		✓	*	N	Y
33	NdBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>		✓		Y	Y
34	SmBaSrCuO <sub>7</sub>		✓		Y	Y
35	EuBaSrCu <sub>3</sub> O <sub>7</sub>		✓		Y	Y
36	BaSrCu <sub>3</sub> O <sub>7</sub>		✓	*	Y	N
37	DyBaSrCu <sub>3</sub> O <sub>7</sub>		✓		Y	Y
38	HuBaSrCu <sub>3</sub> O <sub>7</sub>		✓		Y	Y
39	ErBaSrCu <sub>3</sub> O <sub>7</sub> (Multiphase)		✓		Y	Y
40	TmBaSrCu <sub>3</sub> O <sub>7</sub> (Multiphase)		✓		Y	Y

41	YBaSrCu <sub>3</sub> O <sub>7</sub>		✓	*	Y	Y
42	HgBa <sub>2</sub> CuO <sub>2</sub>		✓	*	Y	N
43	HgBa <sub>2</sub> CaCu <sub>2</sub> O <sub>6</sub> (annealed in O <sub>2</sub> )		✓	*	Y	N
44	HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8</sub>		✓	*	Y	N
45	HgBa <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>10</sub>		✓	*	Y	N

19. The first composition, La<sub>2</sub> Cu O<sub>4+δ</sub>, has the form RE<sub>2</sub>CuO<sub>4</sub> which is explicitly taught by Bednorz and Mueller. The  $\delta$  indicates that there is a nonstoichiometric amount of oxygen.

20. The Bednorz-Mueller application teaches at page 11, line 19 to page 12, line 7:

An example of a superconductive compound having a layer-type structure in accordance with the present invention is an oxide of the general composition RE<sub>2</sub>TMO<sub>4</sub> where RE stands for the rare earths (lanthanides) or rare earth-like elements and TM stands for a transition metal. In these compounds the RE portion can be partially substituted by one or more members of the alkaline earth group of elements. In these particular compounds, the oxygen content is at a deficit. For example, one such compound that meets this general description is lanthanum copper oxide La<sub>2</sub>CuO<sub>4</sub>...

21. The Bednorz-Mueller application at page 15, last paragraph states "Despite their metallic character, the Ba-La-Cu-O type materials are essentially ceramics, as are other compounds of the RE<sub>2</sub> TMO<sub>4</sub> type, and their manufacture generally follows known principles of ceramic fabrication."

22. Compound number 27 of the composite table contains Nd and Ce, both rare earth elements. All of the other compounds of the composite table, except for number 32, have O and one of the alkaline earth elements which as stated above is explicitly taught by applicants. Compound 31 is a BiO<sub>3</sub> compound in which TM is substituted by another element, here Bi, as explicitly taught by Applicants in the paragraph quoted above.

23. The rare earth elements are Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. See the Handbook of Chemistry and Physics 59th edition 1978-1979 page B262 in Appendix A. The transition elements are identified in the periodic table from the inside front cover of the Handbook of Chemistry and Physics in Appendix A.

24. The basic theory of superconductivity has been known many years before Applicants' discovery. For example, see the book "Theory of Superconductivity", M. von Laue, Academic Press, Inc., 1952 (See Attachment AD).

25. In the composite table, compound numbers 7 to 10 and 31 are Bismuth (Bi) compounds. Compound number 12 to 22 are Thallium (Tl) compounds. Compound numbers 23 to 26 are lead (Pb) compounds. Compounds 42 to 45 are Mercury (Hg) compounds. Those compounds that do not come within the scope of an allowed claims (the compounds which are not marked with an asterisk in column 3 of the composite table) are primarily the Bi, Tl, Pb and Hg compounds. These compounds are made according to the principles of ceramic science known prior to applicant's filing date. For example, Attachments J, K, L, and M contain the following articles:

Attachment J - Phys. Rev. B. Vol. 38, No. 16, p. 6531 (1988) is directed to Thallium compounds.

Attachment K - Jap. Joun. of Appl. Phys., Vol. 27, No. 2, p. L209-L210 (1988) is directed to Bismuth (Bi) compounds.

Attachment L - Letter to Nature, Vol. 38, No. 2, p. 226 (18 March 1993) is directed to Mercury (Hg) compounds.

Attachment M - Nature, Vol. 336, p. 211 (17 November 1988) is directed to Lead (Pb) based compounds.

26. The article of Attachment J (directed to Tl compounds) states at page 6531, left column:

The samples were prepared by thoroughly mixing suitable amounts of  $Tl_2O_3$ ,  $CaO$ ,  $BaO_2$ , and  $CuO$ , and forming a pellet of this mixture under pressure. The pellet was then wrapped in gold foil, sealed in quartz tube containing slightly less than 1 atm of oxygen, and baked for approximately 3 h at  $\approx 880^{\circ}C$ .

This is according to the general principles of ceramic science known prior to applicant's priority date.

27. The article of Attachment K (directed to Bi compounds) states at page L209:

The Bi-Sr-Ca-Cu-O oxide samples were prepared from powder reagents of  $Bi_2O_3$ ,  $SrCO_3$ ,  $CaCO_3$  and  $CuO$ . The appropriate amounts of powders were mixed, calcined at  $800-870^{\circ}C$  for 5 h, thoroughly reground and then cold-pressed into disk-shape pellets (20 mm in diameter and 2 mm in thickness) at a pressure of 2 ton. $cm^2$ . Most of the pellets were sintered at about  $870^{\circ}C$  in air or in an oxygen atmosphere and then furnace-cooled to room temperature.

This is according to the general principles of ceramic science known prior to applicant's priority date.

28. The article of Attachment L (directed to Hg compounds) states at page 226:

The samples were prepared by solid state reaction between stoichiometric mixtures of  $\text{Ba}_2\text{CuO}_{3+\delta}$  and yellow  $\text{HgO}$  (98% purity, Aldrich). The precursor  $\text{Ba}_2\text{CuO}_{3+\delta}$  was obtained by the same type of reaction between  $\text{BaO}_2$  (95% purity, Aldrich) and  $\text{CuO}$  (NormalPur, Prolabo) at 930°C in oxygen, according to the procedure described by De Leeuw et al.<sup>6</sup>. The powders were ground in an agate mortar and placed in silica tubes. All these operations were carried out in a dry box. After evacuation, the tubes were sealed, placed in steel containers, as described in ref. 3, and heated for 5 h to reach ~800°C. The samples were then cooled in the furnace, reaching room temperature after ~10 h.

This is according to the general principles of ceramic science known prior to applicant's priority date.

29. The article of Attachment M (directed to Pb compounds) states at page 211, left column:

The preparative conditions for the new materials are considerably more stringent than for the previously known copper-based superconductors. Direct synthesis of members of this family by reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 900°C is not possible because of the stability of the oxidized  $\text{SrPbO}_3$ -based perovskite. Successful synthesis is accomplished by the reaction of  $\text{PbO}$  with pre-reacted ( $\text{Sr}$ ,  $\text{Ca}$ ,  $\text{Ln}$ ) oxide precursors. The precursors are prepared from oxides and carbonates in the appropriate metal ratios, calcined for 16 hours (in dense  $\text{Al}_2\text{O}_3$  crucibles) at 920-980°C in air with one intermediate grinding.

This is according to the principles of ceramic science known prior to applicant's priority date.

30. A person of ordinary skill in the art of the fabrication of ceramic materials would be motivated by the teaching of the Bednorz-Mueller application to investigate compositions for high superconductivity other than the compositions specifically fabricated by Bednorz and Mueller.

31. In Attachment U, there is a list of perovskite materials from pages 191 to 207 in the book "Structure, Properties and Preparation of Perovskite-Type Compounds" by F. S. Galasso, published in 1969, which is Attachment E hereto. This list contains about 300 compounds. Thus, what the term "Perovskite-type" means and how to make these compounds was well known to a person of ordinary skill in the art in 1969, more than 17 years before the Applicants' priority date (January 23, 1987).

This is clear evidence that a person of skill in the art of fabrication of ceramic materials knows (prior to Applicants' priority date) how to make the types of materials in Table 1 of the Rao Article and the Table from the Handbook of Chemistry and Physics as listed in the composite table above in paragraph 17.

32. The standard reference "Landolt-Börnstein", Volumn 4, "Magnetic and Other Properties of Oxides and Related Compounds Part A" (1970) lists at page 148 to 206 Perovskite and Perovskite-related structures. (See Attachment N). Section 3.2 starting at page 190 is entitled "Descriptions of perovskite-related structures". The German title is "Perowskit-ähnliche Strukturen". The German word "ähnliche" can be translated in English as "like". The Langenscheidt's German-English, English-German Dictionary 1970, at page 446 translates the English "like" as the German "ähnliche". (See Attachment O). Pages 126 to 147 of Attachment N describes "crystallographic and magnetic properties of perovskite and perovskite-related compounds", see title of Section 3 at page 126. Section 3.2.3.1 starting at page 192 of "Landolt-Börnstein" Vol. 4 (See Attachment N) is entitled "Bismuth Compounds". Thus Bismuth

perovskite-like compounds and how to make them were well known more than 16 years prior to Applicants' priority date. Thus the "Landolt Börnstein" book published in 1970, more than 16 years before Applicants' priority date (January 23, 1987), shows that the term "perovskite-like" or "perovskite related" is understood by persons of skill in the art prior to Applicants' priority date. Moreover, the "Landolt-Börnstein" book cites references for each compound listed. Thus a person of ordinary skill in the art of ceramic fabrication knows how to make each of these compounds. Pages 376-380 of Attachment N has figures showing the crystal structure of compounds containing Bi and Pb.

33. The standard reference "Landolt-Börnstein, Volume 3, Ferro- and Antiferroelectric Substances" (1969) provides at pages 571-584 an index to substances. (See Attachment P). This list contains numerous Bi and Pb containing compounds. See, for example pages 578 and 582-584. Thus a person of ordinary skill in the art of ceramic fabrication would be motivated by Applicants' application to fabricate Bi and/or Pb containing compounds that come within the scope of the Applicants' claims.

34. The standard reference "Landolt-Börnstein Volume 3 Ferro- and Antiferroelectric Substances" (1969) (See Attachment P) at page 37, section 1 is entitled "Perovskite-type oxides." This standard reference was published more than 17 years before Applicants' priority date (January 23, 1987). The properties of perovskite-type oxides are listed from pages 37 to 88. Thus the term perovskite-type was well known and understood by persons of skill in the art of ceramic fabrication prior to Applicants' priority date and more than 17 years before Applicants' priority date persons of ordinary skill in the art knew how to make Bi, Pb and many other perovskite, perovskite-like, perovskite-related and perovskite-type compounds.

35. At page 14, line 10-15 of the Bednorz-Mueller application, Applicants' state "samples in the Ba-La-Cu-O system, when subjected to x-ray analysis, revealed three individual crystallographic phases V.12. a first layer-type perovskite-like phase, related to the  $K_2NiF_4$  structure ..." Applicants' priority document EP0275343A1 filed July 27, 1988, is entitled "New Superconductive Compounds of the  $K_2NiF_4$  Structural Type Having a High Transition Temperature, and Method for Fabricating Same." See (See Attachment AE). The book "Structure and Properties of Inorganic Solids" by Francis S. Galasso, Pergamon Press (1969) at page 190 lists examples of Taliium (Tl) compounds in the  $K_2NiF_4$  structure. (See Attachment Q). Thus based on Applicants' teachings prior to Applicants' priority date, a person of ordinary skill in the art of ceramic fabrication would be motivated to fabricate Thallium based compounds to test for high  $T_c$  superconductivity.

36. The book "Crystal Structures" Volume 4, by Ralph W. G. Wyckoff, Interscience Publishers, 1960 states at page 96 "This structure, like these of  $Bi_4Ti_2O_{12}$  (IX, F<sub>12</sub>) and  $Ba Bi_4 Ti_4 O_4$  (XI, 13) is built up of alternating  $Bi_2O_2$  and perovskite-like layers." Thus layer of perovskite-like Bismuth compounds was well known in the art in 1960 more than 26 years before Applicants' priority date. (See Attachment R).

37. The book "Modern Oxide Materials Preparation, Properties and Device Applications" edited by Cockayne and Jones, Academic Press (1972) states (See Attachment S) at page 155 under the heading "Layer Structure Oxides and Complex Compounds":

"A large number of layer structure compounds of general formula  $(Bi_2O_2)^{2+}$   $(A_{x-1}B_xO_{3x+1})^2$  have been reported (Smolenskii et al. 1961; Subbarao, 1962), where A = Ca, Sr, Ba, Pb, etc., B = Ti, Nb, Ta and x = 2, 3, 4, or 5. The structure had been previously investigated by Aurivillius (1949) who described them in terms of Alternate  $(Bi_2O_2)^{2+}$  layers and perovskite layers of oxygen octahedra. Few have been found to be ferroelectric and include  $SrBi_2Ta_2O_9$  ( $T_c = 583^\circ K$ ),  $PbBi_2Ta_2O_9$  ( $T_c = 703^\circ K$ ),  $BiBi_3Ti_2TiO_{12}$  or

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$  ( $T_c = 948^\circ\text{K}$ ),  $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  ( $T_c = 598^\circ\text{K}$ ) and  $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  ( $T_c = 583^\circ\text{K}$ ). Only bismuth titanate  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  has been investigated in detail in the single crystal form and is finding applications in optical stores (Cummins, 1967) because of its unique ferroelectric-optical switching properties. The ceramics of other members have some interest because of their dielectric properties. More complex compounds and solid solutions are realizable in these layer structure oxides but none have significant practical application."

Thus the term layered oxides was well known and understood prior to Applicants' priority date. Moreover, layered Bi and Pb compounds were well known in 1972 more than 15 years before Applicants' priority date.

38. The standard reference "Landolt-Börnstein, Volume 3, Ferro and Antiferroelectric Substances" (1969) at pages 107 to 114 (See Attachment T) list "layer-structure oxides" and their properties. Thus the term "layered compounds" was well known in the art of ceramic fabrication in 1969 more than 16 years prior to Applicants' priority date and how to make layered compounds was well known prior to applicants priority date.

39. Layer perovskite type Bi and Pb compounds closely related to the Bi and Pb high  $T_c$  compounds in the composite table above in paragraph 17 have been known for some time. For example, the following is a list of four articles which were published about 35 years prior to Applicants' first publication date:

(1) Attachment V - "Mixed bismuth oxides with layer lattices", B. Aurivillius, Arkiv Kemi 1, 463, (1950).

(2) Attachment W - "Mixed bismuth oxides with layered lattices", B. Aurivillius, Arkiv Kemi 1, 499, (1950).

(3) Attachment X - "Mixed bismuth oxides with layered lattices ", B. Aurivillius, Arkiv Kemi 2, 519, (1951).

(4) Attachment Y - "The structure of  $\text{Bi}_2\text{NbO}_5\text{F}$  and isomorphous compounds", B. Aurivillius, Arkiv Kemi 5, 39, (1952).

These articles will be referred to as Aurivillius 1, 2, 3 and 4, respectively.

40. Attachment V (Aurivillius 1), at page 463, the first page, has the subtitle "I. The structure type of  $\text{CaNb}_2\text{Bi}_2\text{O}_9$ . Attachment V states at page 463:

X-ray analysis ... seemed to show that the structure was built up of  $\text{Bi}_2\text{O}^{2+}$  layers parallel to the basal plane and sheets of composition  $\text{Bi}_2\text{Ti}_3\text{O}^{2-}_{10}$ . The atomic arrangement within the  $\text{Bi}_2\text{Ti}_3\text{O}^{2-}_{10}$  sheets seemed to be the same as in structure of the perovskite type and the structure could then be described as consisting of  $\text{Bi}_2\text{O}^{2+}$  layers between which double perovskite layers are inserted.

41. Attachment V (Aurivillius 1) at page 464 has a section entitled " $\text{PbBi}_2\text{Nb}_2\text{O}_9$  Phase". And at page 471 has a section entitled " $\text{Bi}_3\text{NbTiO}_9$ ". And at page 475 has a table of compounds having the " $\text{CaBi}_2\text{Nb}_2\text{O}_9$  structure" listing the following compounds  $\text{Bi}_3\text{NbTiO}_9$ ,  $\text{Bi}_3\text{TaTiO}_9$ ,  $\text{CaBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{SrBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ,  $\text{BaBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{PbBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{NaBi}_5\text{Nb}_4\text{O}_{18}$ ,  $\text{KBi}_5\text{Nb}_4\text{O}_{18}$ . Thus Bi and Pb layered perovskite compounds were well known in the art about 35 years prior to Applicants' priority date.

42. Attachment W (Aurivillius 2) at page 499, the first page, has the subtitle "II Structure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ". And at page 510, Fig. 4 shows a crystal structure in which "A denotes a perovskite layer  $\text{Bi}_2\text{Ti}_3\text{O}^{2-}_{10}$ , C  $\text{Bi}_2\text{O}^{2+}$  layers and B unit cells of the hypothetical perovskite structure  $\text{BiTiO}_3$ .

43. Attachment X (Aurivillius 3) has at page 519, the first page, the subtitle "III Structure of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ". And in the first paragraph on page 519 states referring to the articles of Attachments V (Aurivillius 1), and W (Aurivillius 2) "X ray studies on the compounds  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  [the article of Attachment V] and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  [the article of Attachment W] have shown that the comparatively complicated chemical formulae of these compounds can be explained by simple layer structures being built up from  $\text{Bi}_2\text{O}_2^-$  layers and perovskite layers. The unit cells are pictured schematically in Figs. 1a and 1c." And Fig. 4 at page 526 shows "One half of a unit cell of  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ . A denotes the perovskite region and B the  $\text{Me}_2\text{O}_4$  layer" where Me represents a metal atom.

44. Attachment Y (Aurivillius 4) is direct to structures having the  $\text{Bi}_3\text{N}_{10}\text{O}_3\text{F}$  structure.

45. Attachment AA is a list of Hg containing solid state compounds from the 1989 Powder Diffraction File Index. Applicants do not have available to them an index from prior to Applicants' priority date. The Powder Diffraction File list is a compilation of all known solid state compounds with reference to articles directed to the properties of these compositions and the methods of fabrication. From Attachment AA it can be seen, for example, that there are numerous examples of Hg based compounds. Similarly, there are examples of other compounds in the Powder Diffraction File. A person of ordinary skill in the art is aware of the Powder Diffraction File and can from this file find a reference providing details on how to fabricate these compounds. Thus persons of ordinary skill in the art would be motivated by Applicants' teaching to look to the Powder Diffraction File for examples of previously fabricated composition expected to have properties similar to those described in Applicants' teaching.

46. It is generally recognized that it is not difficult to fabricate transition metal oxides and in particular copper metal oxides that are superconductive after the discovery by Applicants of composition, such as transition metal oxides, that are high T<sub>c</sub> superconductors. This is noted in the book "Copper Oxide Superconductors" by Charles P. Poole, Jr., Timir Datta and Horacio A. Farach, John Wiley & Sons (1998), referred to herein as Poole 1988: Chapter 5 of Poole 1988 (See Attachment AF) in the book entitled "Preparation and Characterization of Samples" states at page 59 "[c]opper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials". Poole 1988 further states at page 61 "[i]n this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatif). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor." Poole 1988 further states at pages 61-62 "[i]n the solid state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates or carbonates of Ba, Bi, La, Sr, Ti, Y or other elements. ... These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcination for an extended period (~20hr) at elevated temperatures (~900°C). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step." This is generally the same as the specific examples provided by Applicants and as generally described at pages 8, line 19, to page 9, line 5, of the Bednorz-Mueller application which states "[t]he methods by which these superconductive compositions can be made can use known principals of ceramic fabrication, including the mixing of powders containing the rare earth or rare earth-like, alkaline earth, and transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air. A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal."

Consequently, it is my opinion that Applicants have fully enabled high T<sub>c</sub> materials oxides and their claims.

47. Charles Poole et al. published another book in 1995 entitled "Superconductivity" Academic Press which has a Chapter 7 on "Perovskite and Cuprate Crystallographic Structures". (See Attachment Z). This book will be referred to as Poole 1995.

At page 179 of Poole 1995 states:

V. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Mueller (1986) referred to their samples as "metallic, oxygen-deficient ... perovskite-like mixed-valence copper compounds." Subsequent work has confirmed that the new superconductors do indeed possess these characteristics.

I agree with this statement.

48. The book "The New Superconductors", by Frank J. Owens and Charles P. Poole, Plenum Press, 1996, referred to herein as Poole 1996 in Chapter 8 entitled "New High Temperature Superconductors" starting a page 97 (See Attachment AG) shows in Section 8.3 starting at page 98 entitled "Layered Structure of the Cuprates" schematic diagrams of the layered structure of the cuprate superconductors. Poole 1996 states in the first sentence of Section 8.3 at page 98 "All cuprate superconductors have the layered structure shown in Fig. 8.1." This is consistent with the teaching of Bednorz and Mueller that "These compositions have a layer-type Crystalline Structure often Perovskite-like" as noted in paragraph 14 above. Poole 1996 further states in the first sentence of Section 8.3 at page 98 "The flow of supercurrent takes place in conduction layers and bonding layers support and hold together the conduction layers". The caption of Fig. 8.1 states "Layering scheme of the cuprate superconductors". Fig. 8.3 shows details of the conduction layers for difference sequence of copper oxide

planes and Fig. 8.4 presents details of the bonding layers for several of the cuprates which include binding layers for lanthanum superconductor  $\text{La}_2\text{CuO}_4$ , neodymium superconductor  $\text{Nd}_2\text{CuO}_4$ , yttrium superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{2n+4}$ , bismuth superconductor  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , thallium superconductor  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , and mercury superconductor  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ . Fig. 8.5 at pages 102 and 103 show a schematic atomic structure showing the layering scheme for thallium superconductors. Fig. 8.10 at page 109 shows a schematic crystal structure showing the layering scheme for  $\text{La}_2\text{CuO}_4$ . Fig. 8.11 at page 110 shows a schematic crystal structure showing the layering scheme for  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ . The layering shown in Poole 1996 for high  $T_c$  superconductors is consistent with the layering as taught by Bednorz and Mueller in their patent application.

49. Thus Poole 1988 states that the high  $T_c$  superconducting materials "are not difficult to synthesize" and Poole 1995 states that "the new superconductors do indeed possess [the] characteristics" that Applicants' specification describes these new superconductors to have. Poole 1996 provide details showing that high  $T_c$  superconductors are layered or layer-like as taught by Bednorz and Mueller. Therefore, as of Applicants' priority date persons of ordinary skill in the art of ceramic fabrication were enabled to practice Applicants' invention to the full scope that it is presently claimed, including in the claims that are not allowed from the teaching in the Bednorz-Mueller application without undue experimentation that is by following the teaching of Bednorz and Mueller in combination with what was known to persons of ordinary skill in the art of ceramic fabrication. The experiments to make high  $T_c$  superconductors not specifically identified in the Bednorz-Mueller application were made by principles of ceramic fabrication prior to the date of their first publication. It is within the skill of a person of ordinary skill in the art of ceramic fabrication to make compositions according to the teaching of the Bednorz-Mueller application to determine whether or not they are high  $T_c$  superconductors without undue experimentation.

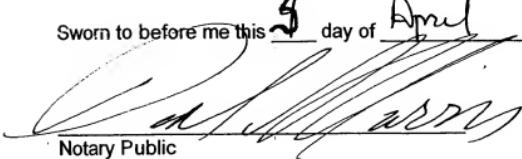
50. I have personally made many samples of high T<sub>c</sub> superconductors following the teaching of Bednorz and Mueller as found in their patent applications. In making these materials it was not necessary to use starting materials in stoichiometric proportions to produce a high T<sub>c</sub> superconductor with insignificant secondary phases or multi-phase compositions, having a superconducting portion and a non-superconducting portion, where the composite was a high T<sub>c</sub> superconductor. Consequently, following the teaching of Bednorz and Mueller and principles of ceramic science known prior to their discovery, I made, and persons of skill in the ceramic arts were able to make, high T<sub>c</sub> superconductors without exerting extreme care in preparing the composition. Thus I made and persons of skill in the ceramic arts were able to make high T<sub>c</sub> superconductors following the teaching of Bednorz and Mueller, without experimentation beyond what was well known to a person of ordinary skill in the ceramic arts prior to the discovery by Bednorz and Mueller.

51. I hereby swear that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or patent issued thereon.

Date: April 5, 2005

By: Chang C. Tsuei  
Chang C. Tsuei

Sworn to before me this 5 day of April, 2005.

  
Notary Public

DANIEL P. MORRIS  
NOTARY PUBLIC, State of New York  
No. 4888676  
Qualified in Westchester County  
Commission Expires March 18, 2007

## **Attachment 1**

Chang C. Tsuei

IBM Thomas J. Watson Research Center  
P.O. Box 218  
Yorktown Heights, NY 10598  
Phone: (914) 945-2799  
Fax: (914) 945-2141

**Education:**

Ph.D. 1966 Materials Science - California Institute of Technology  
M.S. 1963 Materials Science - California Institute of Technology  
B.S. 1960 Mechanical Engineering - National Taiwan University

**Professional Positions:**

*IBM Thomas J. Watson Research Center*

1993 - Present Research Staff Member, Superconductivity  
1983 - 1993 Manager, Physics of Structured Materials  
1979 - 1983 Manager, Physics of Amorphous Materials  
1974 - 1975 Acting Manager, Superconductivity  
1973 - 1979 Research Staff Member

*Universite Paris-Sud*

1996 - 1997 Invited Professor in Solid State Physics

*Harvard University*

1980 (summer) Visiting Scholar in Applied Physics

*Stanford University*

09/1982 -04/1983 Visiting Scholar in Applied Physics

*California Institute of Technology*

1972 - 1973 Senior Research Associate in Applied Physics  
1969 - 1972 Senior Research Fellow in Materials Science  
1966 - 1969 Research Fellow in Materials Science

**Honors:**

2000 Dynamic Achiever Award from the Organization of Chinese Americans  
2000 IBM Corporate Award  
1998 Bodo von Borries Lectureship sponsored by the Bodo von Borries Stiftung of Germany.  
1998 Co-recipient of the Oliver E. Buckley Condensed Matter Physics Prize of the American Physical Society  
1996-1997 Appointment as Invited Professor at the Universite Paris-Sud  
1996 Elected to Academia Sinica  
1996 Academic Achievement Award from the Chinese American Academic and Professional Society  
1995 IBM Outstanding Innovation Award for contributions to the work on half integer flux quantization observed with a scanning SQUID microscope  
1992 Max Planck Research Prize from the Max Planck Society and the Alexander von Humboldt Foundation of Germany  
1990 IBM Outstanding Technical Achievement Award for contributions to the understanding of electrical properties of grain boundaries in high-T<sub>c</sub> superconductors  
1984 IBM Invention Achievement Award

1980 Invention Achievement Award

**Professional Societies Honors:**

2001 Fellow of the American Association for the Advancement of Science

1996 Academician of Academia Sinica

1974 Fellow of American Physical Society

**Publications:** available upon request

**BRIEF ATTACHMENT AO**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: April 5, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated July 28, 2004, please consider the  
following:

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: April 4, 2005

Applicants: Bednorz et al.

Docket: YO987-074BZ

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Filed: June 7, 1995

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For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATIONCommissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450AFFIDAVIT UNDER 37 C.F.R. 1.132

Sir:

I, Timothy Dinger, being duly sworn, do hereby depose and state:

1. I received a B. S. degree in Ceramic Engineering (1981) from New York State College of Ceramics, Alfred University, an M. S. degree (1983) and a Ph.D. degree (1986), both in Material Science from the University of California at Berkeley.
2. I refer to Attachments A to Z and AA herein which were submitted in a separate paper designated as "FIRST SUPPLEMENTAL AMENDMENT" in response to the Office Action dated July 28, 2004. I also refer to Attachments AB to AG which were submitted in a separate paper designated as "THIRD SUPPLEMENTAL AMENDMENT" in response to the Office Action dated July 28, 2004.
3. I have worked as a research staff member in Material Science at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1986 to 2001. From 2001 to the present, I have worked as an I/T Manager in the IBM Chief Information Officer organization.
4. I have worked in the fabrication of and characterization of high temperature superconductor materials from 1987 to 1991.

IBM  
 YORKTOWN  
 2005 APR - 6 PM 1:10  
 PATENT & TRADEMARK OFFICE  
 U.S. GOVERNMENT PRINTING OFFICE  
 WILMINGTON  
 LAW DEPT.

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Serial No.: 08/479,810

Page 1 of 21

Docket: YO987-074BZ

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

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1. I received a B. S. degree in Ceramic Engineering (1981) from New York State College of Ceramics, Alfred University, an M. S. degree (1983) and a Ph.D. degree (1986), both in Material Science from the University of California at Berkeley.
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3. I have worked as a research staff member in Material Science at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1986 to 2001. From 2001 to the present, I have worked as an I/T Manager in the IBM Chief Information Officer organization.
4. I have worked in the fabrication of and characterization of high temperature superconductor materials from 1987 to 1991.

5. My resume and list of publications is in Attachment 1 included with this affidavit.
6. This affidavit is in addition to my affidavit dated December 15, 1998. I have reviewed the above-identified patent application (Bednorz-Mueller application) and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity in a material having a  $T_c \geq 26^{\circ}\text{K}$  and that subsequent developments in this field have been based on this work.
7. All the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner, have similar magnetic properties, and have similar structural properties.
8. Once a person of skill in the art knows of a specific type of composition described in the Bednorz-Mueller application which is superconducting at greater than or equal to  $26^{\circ}\text{K}$ , such a person of skill in the art, using the techniques described in the Bednorz-Mueller application, which includes all principles of ceramic fabrication known at the time the application was initially filed, can make the compositions encompassed by the claims of the Bednorz-Mueller application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art of the fabrication of ceramic materials. This is why the work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period after their discovery. Bednorz and Mueller's discovery was first reported in Z. Phys. B 64 page 189-193 (1996).
9. The techniques for placing a superconductive composition into a superconducting state have been known since the discovery of superconductivity in 1911 by Kamerlingh-Onnes.

10. Prior to 1986 a person having a bachelor's degree in an engineering discipline, applied science, chemistry, physics or a related discipline could have been trained within one year to reliably test a material for the presence of superconductivity and to flow a superconductive current in a superconductive composition.

11. Prior to 1986 a person of ordinary skill in the art of fabricating a composition according to the teaching of the Bednorz-Mueller application would have: a) a Ph.D. degree in solid state chemistry, applied physics, material science, metallurgy, physics or a related discipline and have done thesis research including work in the fabrication of ceramic materials; or b) have a Ph.D. degree in these same fields having done experimental thesis research plus one to two years post Ph.D. work in the fabrication of ceramic materials; or c) have a master's degree in these same fields and have had five years of materials experience at least some of which is in the fabrication of ceramic materials. Such a person is referred to herein as a person of ordinary skill in the ceramic fabrication art.

12. The general principles of ceramic science referred to by Bednorz and Mueller in their patent application and known to a person of ordinary skill in the ceramic fabrication art can be found in many books and articles published before their discovery, priority date (date of filing of their European Patent Office patent application EPO 0275343A1, January 23, 1987) and initial US Application filing date (May 22, 1987). An exemplary list of books describing the general principles of ceramic fabrication are:

- a) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is in Attachment B.
- b) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is in Attachment C.

- c) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is in Attachment D.
- d) Structure, Properties and Preparation of Perovskite-Type Compounds, F. S. Galasso , Pergamon Press, 1969, in particular pages 159-186, a copy of which is in Attachment E.

These references were previously submitted with the Affidavit of Thomas Shaw submitted December 15, 1998.

13. An exemplary list of articles applying the general principles of ceramic fabrication to the types of materials described in Applicants' specification are:

- a) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4+x/2-\epsilon}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981). See Attachment F.
- b) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic (This is referred to in the Bednorz-Mueller application at page 21, lines 1-2) Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985. See Attachment G.
- c) Oxygen Intercalation in Mixed Valence Copper Oxides Related to the Perovskite, C. Michel et al., Revue de Chemie Minerale, 21, p. 407, 1984. (This is referred to in the Bednorz-Mueller application at page 27, lines 1-2). See Attachment H.
- d) Thermal Behaviour of Compositions in the Systems  $x BaTiO_3 + (1-x) Ba(Ln_{0.5} B_{0.5}) O_3$ , V.S. Chincholkar et al., Therm. Anal. 6th, Vol. 2., p. 251-6, 1980. See Attachment I.

14. The Bednorz-Mueller application in the paragraph bridging pages 6 and 7 states in regard to the high T<sub>c</sub> materials:

These compositions can carry supercurrents (i.e., electrical currents in a substantially zero resistance state of the composition) at temperatures greater than 26°K. In general, the compositions are characterized as mixed transition metal oxide systems where the transition metal oxide can exhibit multivalent behavior. These compositions have a layer-type crystalline structure, often perovskite-like, and can contain a rare earth or rare earth-like element. A rare earth-like element (sometimes termed a near rare earth element is one whose properties make it essentially a rare earth element. An example is a group IIIB element of the periodic table, such as La. Substitutions can be found in the rare earth (or rare earth-like) site or in the transition metal sites of the compositions. For example, the rare earth site can also include alkaline earth elements selected from group IIA of the periodic table, or a combination of rare earth or rare earth-like elements and alkaline earth elements. Examples of suitable alkaline earths include Ca, Sr, and Ba. The transition metal site can include a transition metal exhibiting mixed valent behavior, and can include more than one transition metal. A particularly good example of a suitable transition metal is copper. As will be apparent later, Cu-oxide based systems provide unique and excellent properties as high T<sub>c</sub> superconductors. An example of a superconductive composition having high T<sub>c</sub> is the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen. Examples of transition metal elements include Cu, Ni, Cr etc. In particular, transition metals that can exhibit multi-valent states are very suitable. The rare earth elements are typically elements 58-71 of the periodic table, including Ce, Nd, etc.

15. In the passage quoted in paragraph 14 the general formula is RE-TM-O "where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen." This paragraph states "Substitutions can be found in the rare earth (or rare earth-like) site or in the transition metal sites of the compositions. For example, the rare earth site can also include alkaline earth elements selected from group IIA of the periodic table, or a combination of rare earth or rare earth-like elements and alkaline earth elements." Thus applicants teach that RE can be something other than an rare earth. For example, it can be an alkaline earth, but is not limited to a alkaline earth element. It can be an element that has the same effect as an alkaline earth or rare-earth element, that is a rare earth like element. Also, this passage teaches that TM can be substituted with another element, for example, but not limited to, a rare earth, alkaline earth or some other element that acts in place of the transition metal.

16. The following table (in paragraph 18) is compiled from the Table 1 of the Article by Rao (See Attachment AB) and the Table of high T<sub>c</sub> materials from the "CRC Handbook of Chemistry and Physics" 2000-2001 Edition (See Attachment AC). An asterisk in column 5 indicated that the composition of column 2 does not come within the scope of the claims allowed in the Office Action of July 28, 2004.

17. I have reviewed the Office Action dated July 28, 2004, which states at page 6 "The present specification is deemed to be enabled only for compositions comprising a transition metal oxide containing at least a) an alkaline earth element and b) a rare-earth element of Group IIIB element." I disagree for the reasons given herein.

18. Composite Table

1	2	3	4	5	6	7
#	MATERIAL	RAO ARTICLE	HANDBOOK OF CHEM & PHYSICS		ALKALINE EARTH ELEMENT	RARE EARTH ELEMENT
1	La <sub>2</sub> CuO <sub>4+δ</sub>	√	√	*	N	Y
2	La <sub>2-x</sub> Sr <sub>x</sub> (Ba <sub>x</sub> )CuO <sub>4</sub>	√	√		Y	Y
3	La <sub>2</sub> Ca <sub>1-x</sub> Sr <sub>x</sub> Cu <sub>2</sub> O <sub>6</sub>	√	√		Y	Y

4	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	✓	✓		Y	Y
5	YBa <sub>2</sub> Cu <sub>4</sub> O <sub>8</sub>	✓	✓		Y	Y
6	Y <sub>2</sub> Ba <sub>4</sub> Cu <sub>7</sub> O <sub>15</sub>	✓	✓		Y	Y
7	Bi <sub>2</sub> Sr <sub>2</sub> CuO <sub>6</sub>	✓	✓	*	Y	N
8	Bi <sub>2</sub> CaSr <sub>2</sub> Cu <sub>2</sub> O <sub>8</sub>	✓	✓	*	Y	N
9	Bi <sub>2</sub> Ca <sub>2</sub> Sr <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	✓	✓	*	Y	N
10	Bi <sub>2</sub> Sr <sub>2</sub> (Ln <sub>1-x</sub> Ce <sub>x</sub> ) <sub>2</sub> Cu <sub>2</sub> O <sub>10</sub>	✓	✓		Y	Y
11	Tl <sub>2</sub> Ba <sub>2</sub> CuO <sub>6</sub>	✓	✓	*	Y	N
12	Tl <sub>2</sub> CaBa <sub>2</sub> Cu <sub>2</sub> O <sub>8</sub>	✓	✓	*	Y	N
13	Tl <sub>2</sub> Ca <sub>2</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	✓	✓	*	Y	N
14	Tl(BaLa)CuO <sub>5</sub>	✓	✓		Y	Y
15	Tl(SrLa)CuO <sub>5</sub>	✓	✓		Y	Y
16	(Tl <sub>0.5</sub> Pb <sub>0.5</sub> )Sr <sub>2</sub> CuO <sub>5</sub>	✓	✓	*	Y	N
17	TlCaBa <sub>2</sub> Cu <sub>2</sub> O <sub>7</sub>	✓	✓	*	Y	N
18	(Tl <sub>0.5</sub> Pb <sub>0.5</sub> )CaSr <sub>2</sub> Cu <sub>2</sub> O <sub>7</sub>	✓	✓	*	Y	N
19	TlSr <sub>2</sub> Y <sub>0.5</sub> Ca <sub>0.5</sub> Cu <sub>2</sub> O <sub>7</sub>	✓	✓		Y	Y
20	TlCa <sub>2</sub> Ba <sub>2</sub> Cu <sub>3</sub> O <sub>8</sub>	✓	✓	*	Y	N
21	(Tl <sub>0.5</sub> Pb <sub>0.5</sub> )Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>9</sub>	✓	✓	*	Y	N
22	TlBa <sub>2</sub> (Ln <sub>1-x</sub> Ce <sub>x</sub> ) <sub>2</sub> Cu <sub>2</sub> O <sub>9</sub>	✓	✓		Y	Y
23	Pb <sub>2</sub> Sr <sub>2</sub> Ln <sub>0.5</sub> Ca <sub>0.5</sub> Cu <sub>3</sub> O <sub>8</sub>	✓	✓		Y	Y
24	Pb <sub>2</sub> (Sr,La) <sub>2</sub> Cu <sub>2</sub> O <sub>6</sub>	✓	✓		Y	Y
25	(Pb,Cu)Sr <sub>2</sub> (Ln,Ca)Cu <sub>2</sub> O <sub>7</sub>	✓	✓		Y	Y
26	(Pb,Cu)(Sr,Eu)(Eu,Ce)Cu <sub>2</sub> O <sub>x</sub>	✓	✓		Y	Y
27	Nd <sub>2-x</sub> Ce <sub>x</sub> CuO <sub>4</sub>	✓	✓	*	N	Y
28	Ca <sub>1-x</sub> Nd <sub>x</sub> CuO <sub>2</sub>	✓			Y	Y
29	Sr <sub>1-x</sub> Nd <sub>x</sub> CuO <sub>2</sub>	✓	✓		Y	Y
30	Ca <sub>1-x</sub> Sr <sub>x</sub> CuO <sub>2</sub>	✓		*	Y	N
31	Ba <sub>0.6</sub> K <sub>0.4</sub> BiO <sub>3</sub>	✓		*	Y	N
32	Rb <sub>2</sub> C <sub>5</sub> C <sub>60</sub>	✓		*	N	Y
33	NdBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	✓			Y	Y
34	SmBaSrCuO <sub>7</sub>	✓			Y	Y
35	EuBaSrCu <sub>3</sub> O <sub>7</sub>	✓			Y	Y
36	BaSrCu <sub>3</sub> O <sub>7</sub>	✓		*	Y	N
37	DyBaSrCu <sub>3</sub> O <sub>7</sub>	✓			Y	Y
38	HuBaSrCu <sub>3</sub> O <sub>7</sub>	✓			Y	Y
39	ErBaSrCu <sub>3</sub> O <sub>7</sub> (Multiphase)	✓			Y	Y
40	TmBaSrCu <sub>3</sub> O <sub>7</sub> (Multiphase)		✓		Y	Y

41	YBaSrCu <sub>3</sub> O <sub>7</sub>		✓	*	Y	Y
42	HgBa <sub>2</sub> CuO <sub>2</sub>		✓	*	Y	N
43	HgBa <sub>2</sub> CaCu <sub>2</sub> O <sub>6</sub> (annealed in O <sub>2</sub> )		✓	*	Y	N
44	HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8</sub>		✓	*	Y	N
45	HgBa <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>10</sub>		✓	*	Y	N

19. The first composition, La<sub>2</sub> Cu O<sub>4+δ</sub>, has the form RE<sub>2</sub>CuO<sub>4</sub> which is explicitly taught by Bednorz and Mueller. The δ indicates that there is a nonstoichiometric amount of oxygen.

20. The Bednorz-Mueller application teaches at page 11, line 19 to page 12, line 7:

An example of a superconductive compound having a layer-type structure in accordance with the present invention is an oxide of the general composition RE<sub>2</sub>TMO<sub>4</sub> where RE stands for the rare earths (lanthanides) or rare earth-like elements and TM stands for a transition metal. In these compounds the RE portion can be partially substituted by one or more members of the alkaline earth group of elements. In these particular compounds, the oxygen content is at a deficit. For example, one such compound that meets this general description is lanthanum copper oxide La<sub>2</sub>CuO<sub>4</sub>...

21. The Bednorz-Mueller application at page 15, last paragraph states "Despite their metallic character, the Ba-La-Cu-O type materials are essentially ceramics, as are other compounds of the RE<sub>2</sub> TMO<sub>4</sub> type, and their manufacture generally follows known principles of ceramic fabrication."

22. Compound number 27 of the composite table contains Nd and Ce, both rare earth elements. All of the other compounds of the composite table, except for number 32, have O and one of the alkaline earth elements which as stated above is explicitly taught by applicants. Compound 31 is a BiO<sub>3</sub> compound in which TM is substituted by another element, here Bi, as explicitly taught by Applicants in the paragraph quoted above.

23. The rare earth elements are Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. See the Handbook of Chemistry and Physics 59th edition 1978-1979 page B262 in Appendix A. The transition elements are identified in the periodic table from the inside front cover of the Handbook of Chemistry and Physics in Appendix A.

24. The basic theory of superconductivity has been known many years before Applicants' discovery. For example, see the book "Theory of Superconductivity", M. von Laue, Academic Press, Inc., 1952 (See Attachment AD).

25. In the composite table, compound numbers 7 to 10 and 31 are Bismuth (Bi) compounds. Compound number 12 to 22 are Thallium (Tl) compounds. Compound numbers 23 to 26 are lead (Pb) compounds. Compounds 42 to 45 are Mercury (Hg) compounds. Those compounds that do not come within the scope of an allowed claims (the compounds which are not marked with an asterisk in column 3 of the composite table) are primarily the Bi, Tl, Pb and Hg compounds. These compounds are made according to the principles of ceramic science known prior to applicant's filing date. For example, Attachments J, K, L, and M contain the following articles:

Attachment J - Phys. Rev. B. Vol. 38, No. 16, p. 6531 (1988) is directed to Thallium compounds.

Attachment K - Jap. Joun. of Appl. Phys., Vol. 27, No. 2, p. L209-L210 (1988) is directed to Bismuth (Bi) compounds.

Attachment L - Letter to Nature, Vol. 38, No. 2, p. 226 (18 March 1993) is directed to Mercury (Hg) compounds.

Attachment M - Nature, Vol. 336, p. 211 (17 November 1988) is directed to Lead (Pb) based compounds.

26. The article of Attachment J (directed to Tl compounds) states at page 6531, left column:

The samples were prepared by thoroughly mixing suitable amounts of  $Tl_2O_3$ ,  $CaO$ ,  $BaO_2$ , and  $CuO$ , and forming a pellet of this mixture under pressure. The pellet was then wrapped in gold foil, sealed in quartz tube containing slightly less than 1 atm of oxygen, and baked for approximately 3 h at  $\approx 880^{\circ}C$ .

This is according to the general principles of ceramic science known prior to applicant's priority date.

27. The article of Attachment K (directed to Bi compounds) states at page L209:

The Bi-Sr-Ca-Cu-O oxide samples were prepared from powder reagents of  $Bi_2O_3$ ,  $SrCO_3$ ,  $CaCO_3$  and  $CuO$ . The appropriate amounts of powders were mixed, calcined at  $800\text{-}870^{\circ}C$  for 5 h, thoroughly reground and then cold-pressed into disk-shape pellets (20 mm in diameter and 2 mm in thickness) at a pressure of 2 ton.cm<sup>2</sup>. Most of the pellets were sintered at about  $870^{\circ}C$  in air or in an oxygen atmosphere and then furnace-cooled to room temperature.

This is according to the general principles of ceramic science known prior to applicant's priority date.

28. The article of Attachment L (directed to Hg compounds) states at page 226:

The samples were prepared by solid state reaction between stoichiometric mixtures of  $\text{Ba}_2\text{CuO}_{3+\delta}$  and yellow  $\text{HgO}$  (98% purity, Aldrich). The precursor  $\text{Ba}_2\text{CuO}_{3+\delta}$  was obtained by the same type of reaction between  $\text{BaO}_2$  (95% purity, Aldrich) and  $\text{CuO}$  (NormalPur, Prolabo) at 930°C in oxygen, according to the procedure described by De Leeuw et al.<sup>6</sup>. The powders were ground in an agate mortar and placed in silica tubes. All these operations were carried out in a dry box. After evacuation, the tubes were sealed, placed in steel containers, as described in ref. 3, and heated for 5 h to reach ~800°C. The samples were then cooled in the furnace, reaching room temperature after ~10 h.

This is according to the general principles of ceramic science known prior to applicant's priority date.

29. The article of Attachment M (directed to Pb compounds) states at page 211, left column:

The preparative conditions for the new materials are considerably more stringent than for the previously known copper-based superconductors. Direct synthesis of members of this family by reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 900°C is not possible because of the stability of the oxidized  $\text{SrPbO}_3$ -based perovskite. Successful synthesis is accomplished by the reaction of  $\text{PbO}$  with pre-reacted ( $\text{Sr}$ ,  $\text{Ca}$ ,  $\text{Ln}$ ) oxide precursors. The precursors are prepared from oxides and carbonates in the appropriate metal ratios, calcined for 16 hours (in dense  $\text{Al}_2\text{O}_3$  crucibles) at 920-980°C in air with one intermediate grinding.

This is according to the principles of ceramic science known prior to applicant's priority date.

30. A person of ordinary skill in the art of the fabrication of ceramic materials would be motivated by the teaching of the Bednorz-Mueller application to investigate compositions for high superconductivity other than the compositions specifically fabricated by Bednorz and Mueller.

31. In Attachment U, there is a list of perovskite materials from pages 191 to 207 in the book "Structure, Properties and Preparation of Perovskite-Type Compounds" by F. S. Galasso, published in 1969, which is Attachment E hereto. This list contains about 300 compounds. Thus, what the term "Perovskite-type" means and how to make these compounds was well known to a person of ordinary skill in the art in 1969, more than 17 years before the Applicants' priority date (January 23, 1987).

This is clear evidence that a person of skill in the art of fabrication of ceramic materials knows (prior to Applicants' priority date) how to make the types of materials in Table 1 of the Rao Article and the Table from the Handbook of Chemistry and Physics as listed in the composite table above in paragraph 17.

32. The standard reference "Landolt-Börnstein", Volumn 4, "Magnetic and Other Properties of Oxides and Related Compounds Part A" (1970) lists at page 148 to 206 Perovskite and Perovskite-related structures. (See Attachment N). Section 3.2 starting at page 190 is entitled "Descriptions of perovskite-related structures". The German title is "Perowskit-ähnliche Strukturen." The German word "ähnliche" can be translated in English as "like". The Langenscheidt's German-English, English-German Dictionary 1970, at page 446 translates the English "like" as the German "ähnliche". (See Attachment O). Pages 126 to 147 of Attachment N describes "crystallographic and magnetic properties of perovskite and perovskite-related compounds", see title of Section 3 at page 126. Section 3.2.3.1 starting at page 192 of "Landolt-Börnstein" Vol. 4 (See Attachment N) is entitled "Bismuth Compounds". Thus Bismuth

perovskite-like compounds and how to make them were well known more than 16 years prior to Applicants' priority date. Thus the "Landolt Börnstein" book published in 1970, more than 16 years before Applicants' priority date (January 23, 1987), shows that the term "perovskite-like" or "perovskite related" is understood by persons of skill in the art prior to Applicants' priority date. Moreover, the "Landolt-Börnstein" book cites references for each compound listed. Thus a person of ordinary skill in the art of ceramic fabrication knows how to make each of these compounds. Pages 376-380 of Attachment N has figures showing the crystal structure of compounds containing Bi and Pb.

33. The standard reference "Landolt-Börnstein, Volume 3, Ferro- and Antiferroelectric Substances" (1969) provides at pages 571-584 an index to substances. (See Attachment P). This list contains numerous Bi and Pb containing compounds. See, for example pages 578 and 582-584. Thus a person of ordinary skill in the art of ceramic fabrication would be motivated by Applicants' application to fabricate Bi and/or Pb containing compounds that come within the scope of the Applicants' claims.

34. The standard reference "Landolt-Börnstein Volume 3 Ferro- and Antiferroelectric Substances" (1969) (See Attachment P) at page 37, section 1 is entitled "Perovskite-type oxides." This standard reference was published more than 17 years before Applicants' priority date (January 23, 1987). The properties of perovskite-type oxides are listed from pages 37 to 88. Thus the term perovskite-type was well known and understood by persons of skill in the art of ceramic fabrication prior to Applicants' priority date and more than 17 years before Applicants' priority date persons of ordinary skill in the art knew how to make Bi, Pb and many other perovskite, perovskite-like, perovskite-related and perovskite-type compounds.

35. At page 14, line 10-15 of the Bednorz-Mueller application, Applicants' state "samples in the Ba-La-Cu-O system, when subjected to x-ray analysis, revealed three individual crystallographic phases V.12. a first layer-type perovskite-like phase, related to the  $K_2NiF_4$  structure ..." Applicants' priority document EP0275343A1 filed July 27, 1988, is entitled "New Superconductive Compounds of the  $K_2NiF_4$  Structural Type Having a High Transition Temperature, and Method for Fabricating Same." See (See Attachment AE). The book "Structure and Properties of Inorganic Solids" by Francis S. Galasso, Pergamon Press (1969) at page 190 lists examples of Taliium (Tl) compounds in the  $K_2NiF_4$  structure. (See Attachment Q). Thus based on Applicants' teachings prior to Applicants' priority date, a person of ordinary skill in the art of ceramic fabrication would be motivated to fabricate Thallium based compounds to test for high  $T_c$  superconductivity.

36. The book "Crystal Structures" Volume 4, by Ralph W. G. Wyckoff, Interscience Publishers, 1960 states at page 96 "This structure, like these of  $Bi_4Ti_2O_{12}$  (IX, F<sub>12</sub>) and  $Ba_2Bi_4Ti_4O_9$  (XI, 13) is built up of alternating  $Bi_2O_2$  and perovskite-like layers." Thus layer of perovskite-like Bismuth compounds was well known in the art in 1960 more than 26 years before Applicants' priority date. (See Attachment R).

37. The book "Modern Oxide Materials Preparation, Properties and Device Applications" edited by Cockayne and Jones, Academic Press (1972) states (See Attachment S) at page 155 under the heading "Layer Structure Oxides and Complex Compounds":

"A large number of layer structure compounds of general formula  $(Bi_2O_2)^{2+} (A_xBi_xO_{3x+1})^{2-}$  have been reported (Smolenskii et al. 1961; Subbarao, 1962), where A = Ca, Sr, Ba, Pb, etc., B = Ti, Nb, Ta and x = 2, 3, 4, or 5. The structure had been previously investigated by Aurivillius (1949) who described them in terms of Alternate  $(Bi_2O_2)^{2+}$  layers and perovskite layers of oxygen octahedra. Few have been found to be ferroelectric and include  $SrBi_2Ta_2O_9$  ( $T_c = 583^\circ K$ ),  $PbBi_2Ta_2O_9$  ( $T_c = 703^\circ K$ ),  $BiBi_3Ti_2TiO_{12}$  or

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$  ( $T_c = 948^\circ\text{K}$ ),  $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  ( $T_c = 598^\circ\text{K}$ ) and  $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  ( $T_c = 583^\circ\text{K}$ ). Only bismuth titanate  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  has been investigated in detail in the single crystal form and is finding applications in optical stores (Cummins, 1967) because of its unique ferroelectric-optical switching properties. The ceramics of other members have some interest because of their dielectric properties. More complex compounds and solid solutions are realizable in these layer structure oxides but none have significant practical application."

Thus the term layered oxides was well known and understood prior to Applicants' priority date. Moreover, layered Bi and Pb compounds were well known in 1972 more than 15 years before Applicants' priority date.

38. The standard reference "Landolt-Börnstein, Volume 3, Ferro and Antiferroelectric Substances" (1969) at pages 107 to 114 (See Attachment T) list "layer-structure oxides" and their properties. Thus the term "layered compounds" was well known in the art of ceramic fabrication in 1969 more than 16 years prior to Applicants' priority date and how to make layered compounds was well known prior to applicants priority date.

39. Layer perovskite type Bi and Pb compounds closely related to the Bi and Pb high  $T_c$  compounds in the composite table above in paragraph 17 have been known for some time. For example, the following is a list of four articles which were published about 35 years prior to Applicants' first publication date:

(1) Attachment V - "Mixed bismuth oxides with layer lattices", B. Aurivillius, Arkiv Kemi 1, 463, (1950).

(2) Attachment W - "Mixed bismuth oxides with layered lattices ", B. Aurivillius, Arkiv Kemi 1, 499, (1950).

(3) Attachment X - "Mixed bismuth oxides with layered lattices ", B. Aurivillius, Arkiv Kemi 2, 519, (1951).

(4) Attachment Y - "The structure of  $\text{Bi}_2\text{NbO}_5\text{F}$  and isomorphous compounds", B. Aurivillius, Arkiv Kemi 5, 39, (1952).

These articles will be referred to as Aurivillius 1, 2, 3 and 4, respectively.

40. Attachment V (Aurivillius 1), at page 463, the first page, has the subtitle "I. The structure type of  $\text{CaNb}_2\text{Bi}_2\text{O}_9$ . Attachment V states at page 463:

X-ray analysis ... seemed to show that the structure was built up of  $\text{Bi}_2\text{O}_2^+$  layers parallel to the basal plane and sheets of composition  $\text{Bi}_2\text{Ti}_3\text{O}^{2-}_{10}$ . The atomic arrangement within the  $\text{Bi}_2\text{Ti}_3\text{O}^{2-}_{10}$  sheets seemed to be the same as in structure of the perovskite type and the structure could then be described as consisting of  $\text{Bi}_2\text{O}_2^+$  layers between which double perovskite layers are inserted.

41. Attachment V (Aurivillius 1) at page 464 has a section entitled " $\text{PbBi}_2\text{Nb}_2\text{O}_9$  Phase". And at page 471 has a section entitled " $\text{Bi}_3\text{NbTiO}_9$ ". And at page 475 has a table of compounds having the " $\text{CaBi}_2\text{Nb}_2\text{O}_9$  structure" listing the following compounds  $\text{Bi}_3\text{NbTiO}_9$ ,  $\text{Bi}_3\text{TaTiO}_9$ ,  $\text{CaBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{SrBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ,  $\text{BaBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{PbBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{NaBi}_3\text{Nb}_4\text{O}_{18}$ ,  $\text{KBi}_3\text{Nb}_4\text{O}_{18}$ . Thus Bi and Pb layered perovskite compounds were well known in the art about 35 years prior to Applicants' priority date.

42. Attachment W (Aurivillius 2) at page 499, the first page, has the subtitle "II Structure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ". And at page 510, Fig. 4 shows a crystal structure in which "A denotes a perovskite layer  $\text{Bi}_2\text{Ti}_3\text{O}^{2-}_{10}$ , C  $\text{Bi}_2\text{O}_2^+$  layers and B unit cells of the hypothetical perovskite structure  $\text{BiTiO}_3$ .

43. Attachment X (Aurivillius 3) has at page 519, the first page, the subtitle "III Structure of BaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>". And in the first paragraph on page 519 states referring to the articles of Attachments V (Aurivillius 1), and W (Aurivillius 2) "X ray studies on the compounds CaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> [the article of Attachment V] and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> [the article of Attachment W] have shown that the comparatively complicated chemical formulae of these compounds can be explained by simple layer structures being built up from Bi<sub>2</sub>O<sub>2</sub><sup>+</sup> layers and perovskite layers. The unit cells are pictured schematically in Figs. 1a and 1c." And Fig. 4 at page 526 shows "One half of a unit cell of BaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>. A denotes the perovskite region and B the Me<sub>2</sub>O<sub>4</sub> layer" where Me represents a metal atom.

44. Attachment Y (Aurivillius 4) is direct to structures having the Bi<sub>3</sub>N<sub>10</sub>O<sub>9</sub>F structure.

45. Attachment AA is a list of Hg containing solid state compounds from the 1989 Powder Diffraction File Index. Applicants do not have available to them an index from prior to Applicants' priority date. The Powder Diffraction File list is a compilation of all known solid state compounds with reference to articles directed to the properties of these compositions and the methods of fabrication. From Attachment AA it can be seen, for example, that there are numerous examples of Hg based compounds. Similarly, there are examples of other compounds in the Powder Diffraction File. A person of ordinary skill in the art is aware of the Powder Diffraction File and can from this file find a reference providing details on how to fabricate these compounds. Thus persons of ordinary skill in the art would be motivated by Applicants' teaching to look to the Powder Diffraction File for examples of previously fabricated composition expected to have properties similar to those described in Applicants' teaching.

46. It is generally recognized that it is not difficult to fabricate transition metal oxides and in particular copper metal oxides that are superconductive after the discovery by Applicants of composition, such as transition metal oxides, that are high T<sub>c</sub> superconductors. This is noted in the book "Copper Oxide Superconductors" by Charles P. Poole, Jr., Timir Datta and Horacio A. Farach, John Wiley & Sons (1998), referred to herein as Poole 1988: Chapter 5 of Poole 1988 (See Attachment AF) in the book entitled "Preparation and Characterization of Samples" states at page 59 "[c]opper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials". Poole 1988 further states at page 61 "[i]n this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor." Poole 1988 further states at pages 61-62 "[i]n the solid state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates or carbonates of Ba, Bi, La, Sr, Ti, Y or other elements. ... These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcination for an extended period (~20hr) at elevated temperatures (~900°C). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step." This is generally the same as the specific examples provided by Applicants and as generally described at pages 8, line 19, to page 9, line 5, of the Bednorz-Mueller application which states "[t]he methods by which these superconductive compositions can be made can use known principals of ceramic fabrication, including the mixing of powders containing the rare earth or rare earth-like, alkaline earth, and transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air. A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal."

Consequently, it is my opinion that Applicants have fully enabled high T<sub>c</sub> materials oxides and their claims.

47. Charles Poole et al. published another book in 1995 entitled "Superconductivity" Academic Press which has a Chapter 7 on "Perovskite and Cuprate Crystallographic Structures". (See Attachment Z). This book will be referred to as Poole 1995.

At page 179 of Poole 1995 states:

#### V. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Mueller (1986) referred to their samples as "metallic, oxygen-deficient ... perovskite-like mixed-valence copper compounds." Subsequent work has confirmed that the new superconductors do indeed possess these characteristics.

I agree with this statement.

48. The book "The New Superconductors", by Frank J. Owens and Charles P. Poole, Plenum Press, 1996, referred to herein as Poole 1996 in Chapter 8 entitled "New High Temperature Superconductors" starting a page 97 (See Attachment AG) shows in Section 8.3 starting at page 98 entitled "Layered Structure of the Cuprates" schematic diagrams of the layered structure of the cuprate superconductors. Poole 1996 states in the first sentence of Section 8.3 at page 98 "All cuprate superconductors have the layered structure shown in Fig. 8.1." This is consistent with the teaching of Bednorz and Mueller that "These compositions have a layer-type Crystalline Structure often Perovskite-like" as noted in paragraph 14 above. Poole 1996 further states in the first sentence of Section 8.3 at page 98 "The flow of supercurrent takes place in conduction layers and bonding layers support and hold together the conduction layers". The caption of Fig. 8.1 states "Layering scheme of the cuprate superconductors". Fig. 8.3 shows details of the conduction layers for difference sequence of copper oxide

planes and Fig. 8.4 presents details of the bonding layers for several of the cuprates which include binding layers for lanthanum superconductor  $\text{La}_2\text{CuO}_4$ , neodymium superconductor  $\text{Nd}_2\text{CuO}_4$ , yttrium superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{2n+4}$ , bismuth superconductor  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , thallium superconductor  $\text{Tl}_2\text{Ba}_2\text{Ca}_n\text{Cu}_n\text{O}_{2n+4}$ , and mercury superconductor  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ . Fig. 8.5 at pages 102 and 103 show a schematic atomic structure showing the layering scheme for thallium superconductors. Fig. 8.10 at page 109 shows a schematic crystal structure showing the layering scheme for  $\text{La}_2\text{CuO}_4$ . Fig. 8.11 at page 110 shows a schematic crystal structure showing the layering scheme for  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{6+x}$ . The layering shown in Poole 1996 for high  $T_c$  superconductors is consistent with the layering as taught by Bednorz and Mueller in their patent application.

49. Thus Poole 1988 states that the high  $T_c$  superconducting materials "are not difficult to synthesize" and Poole 1995 states that "the new superconductors do indeed possess [the] characteristics" that Applicants' specification describes these new superconductors to have. Poole 1996 provide details showing that high  $T_c$  superconductors are layered or layer-like as taught by Bednorz and Mueller. Therefore, as of Applicants' priority date persons of ordinary skill in the art of ceramic fabrication were enabled to practice Applicants' invention to the full scope that it is presently claimed, including in the claims that are not allowed from the teaching in the Bednorz-Mueller application without undue experimentation that is by following the teaching of Bednorz and Mueller in combination with what was known to persons of ordinary skill in the art of ceramic fabrication. The experiments to make high  $T_c$  superconductors not specifically identified in the Bednorz-Mueller application were made by principles of ceramic fabrication prior to the date of their first publication. It is within the skill of a person of ordinary skill in the art of ceramic fabrication to make compositions according to the teaching of the Bednorz-Mueller application to determine whether or not they are high  $T_c$  superconductors without undue experimentation.

50. I have personally made many samples of high T<sub>c</sub> superconductors following the teaching of Bednorz and Mueller as found in their patent applications. In making these materials it was not necessary to use starting materials in stoichiometric proportions to produce a high T<sub>c</sub> superconductor with insignificant secondary phases or multi-phase compositions, having a superconducting portion and a non-superconducting portion, where the composite was a high T<sub>c</sub> superconductor. Consequently, following the teaching of Bednorz and Mueller and principles of ceramic science known prior to their discovery, I made, and persons of skill in the ceramic arts were able to make, high T<sub>c</sub> superconductors without exerting extreme care in preparing the composition. Thus I made and persons of skill in the ceramic arts were able to make high T<sub>c</sub> superconductors following the teaching of Bednorz and Mueller, without experimentation beyond what was well known to a person of ordinary skill in the ceramic arts prior to the discovery by Bednorz and Mueller.

51. I hereby swear that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or patent issued thereon.

Date: April 4, 2005

By: Timothy R. Diriger  
Timothy Diriger

Sworn to before me this 4<sup>th</sup> day of April, 2005.

Eileen C. Daly  
Notary Public

Eileen C. Daly  
Notary Public, State of New York  
No. of ID A5037543  
Qualified in Dutchess County  
Commission Expires February 20 2007

50. I have personally made many samples of high T<sub>c</sub> superconductors following the teaching of Bednorz and Mueller as found in the patent applications. In making these materials it was not necessary to use starting materials in stoichiometric proportions to produce a high T<sub>c</sub> superconductor with insignificant secondary phases or multi-phase compositions, having a superconducting portion and a non-superconducting portion, where the composite was a high T<sub>c</sub> superconductor. Consequently, following the teaching of Bednorz and Mueller and principles of ceramic science known prior to their discovery, I made, and persons of skill in the ceramic arts were able to make, high T<sub>c</sub> superconductors without exerting extreme care in preparing the composition. Thus I made and persons of skill in the ceramic arts were able to make high T<sub>c</sub> superconductors following the teaching of Bednorz and Mueller, without experimentation beyond what was well known to a person of ordinary skill in the ceramic arts prior to the discovery by Bednorz and Mueller.

51. I hereby swear that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or patent issued thereon.

Date: April 4, 2005

By: Timothy R. Diriger  
Timothy Diriger

Sworn to before me this 4<sup>th</sup> day of April, 2005.

Ileen C. Daly  
Notary Public

Eileen C. Daly  
Notary Public State of New York  
No. 02C-47537545  
Qualified in Dutchess County  
Commission Expires February 20 2007

**Attachment 1**

*Timothy R. Dinger*  
*IBM Corporate Headquarters*  
*Enterprise On Demand Transformation and CIO Organization*  
*294 Route 100*  
*Somers, NY 10589*

Telephone: (914) 766-3507  
FAX: (914) 766-7145  
e-mail address: dinger@us.ibm.com

#### **Title**

IBM Corporate Headquarters, Enterprise On Demand Transformation and CIO Organization - Manager, B2B Technology Strategy and Architecture, (2001 - present). Responsibility to define B2B technology strategy and architecture for IBM's On Demand Infrastructure and reduce that strategy to practice by developing and maintaining IBM's edge-of-enterprise B2B Gateway in support of the IBM Business Unit B2B strategies.

#### **Education**

Ph.D. (1986) - Materials Science and Engineering, University of California at Berkeley  
M.S. (1983) - Materials Science and Engineering, University of California at Berkeley  
B.S. (1981) - Ceramic Engineering, Alfred University

#### **Professional Experience**

Information Systems Department, IBM Research Division, Yorktown Heights, NY, Senior Manager/Research Staff Member - Watson Information Systems, (1998-2001). Responsibilities included financial planning and decision-making for IBM's worldwide Research Division (8 laboratories worldwide) and formation of and coordination of the Research Division's program to influence and support the goals of the IBM CIO.

Information Systems Department, IBM Research Division, Yorktown Heights, NY, Manager/Research Staff Member - Server Systems Engineering, (1997 - 1998).

Physical Sciences Department, IBM Research Division, Yorktown Heights, NY, Manager/Research Staff Member - Center for Scalable Computing Solutions, (1994-1996).

Semiconductor Research and Development Center, IBM Microelectronics Division, East Fishkill, NY, Manager/Research Staff Member - Advanced Logic Interconnection Technology, (1993-1994).

Semiconductor Research and Development Center, IBM Microelectronics Division, East Fishkill, NY, Technical Assistant to John E. Kelly III, the Director of the SRDC (1993).

IBM Thomas J. Watson Research Center, Yorktown Heights, NY, Manager/Research Staff Member, Interconnection Performance and Reliability Group, Semiconductor Research and Development Center (1991 - 1993).

IBM T.J. Watson Research Center, Research Staff Member, Ceramic Materials Group, System Technology and Science Department (1987 - 1991).

IBM T.J. Watson Research Center, Postdoctoral Fellow, Exploratory Packaging Materials and Processes Group, Semiconductor Science and Technology Department (1986-1987).

University of California, Berkeley, CA, Graduate Student Research Assistant (1981-1985).

Lawrence Livermore National Laboratory, Livermore, CA, Research Assistant, Ceramic Science Group (1981).

**Selected Publications** (currently author/coauthor of 47 publications, 5 U.S. Patents)

T.P. Smith III, T.R. Dinger, D.C. Edelstein, J.R. Paraszczak, and T.H. Ning, "The Wiring Challenge: Complexity and Crowding," *Future Trends in Microelectronics: Reflections on the Road to Nanotechnology*, S. Luryi, J. Xu, and A. Zaslavsky, eds. NATO ASI Series, Vol. 323, Kluwer Academic Publishers, Boston, pp. 45-56, 1996.

T.R. Dinger, T.K. Worthington, W.J. Gallagher and R.L. Sandstrom, "Direct Observation of Electronic Anisotropy in Single-Crystal  $Y_1Ba_2Cu_3O_x$ ," *Phys. Rev. Lett.*, **58**, [25], 2687-2690(1987).

T.K. Worthington, W.J. Gallagher, and T.R. Dinger, "Anisotropic Nature of High-Temperature Superconductivity in Single-Crystal  $Y_1Ba_2Cu_3O_{7-x}$ ," *Phys. Rev. Lett.*, **59**, [10], 1160-1163(1987).

T.R. Dinger and S.W. Tozer, "Old Behaviour in New Materials," *Nature*, **332**, 204, 17 March 1988.

T.R. Dinger, R.S. Rai and G. Thomas, "Crystallization Behavior of a Glass in the  $Y_2O_3$ - $SiO_2$ -AlN System," *J. Am. Cer. Soc.*, **71**, [4], 236-44(1988).

G.J. Dolan, G.V. Chandrashekhar, T.R. Dinger, C. Feild and F. Holtzberg, "Vortex Structure in  $YBa_2Cu_3O_7$  and Evidence for Intrinsic Pinning," *Phys. Rev. Lett.*, **62**, [7], 827-830(1989).

G.J. Dolan, F. Holtzberg, C. Feild, and T.R. Dinger, "Anisotropic Vortex Structure in  $Y_1Ba_2Cu_3O_7$ ," *Phys. Rev. Lett.*, **62**, [18], 2184-2187(1989).

T.R. Dinger, G.J. Dolan, D. Keane, T.R. McGuire, T.K. Worthington, R.M. Yandrofski and Y. Yeshurun, "Flux Pinning in Single-Crystal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ," High Temperature Superconducting Compounds: Processing and Related Properties, Proceedings of the 1989 Symposium on High Temperature Superconducting Oxides: Processing and Related Properties, 118th Annual Meeting of TMS-AIME, Las Vegas, Nevada, February 27 - March 3, 1989, Edited by S.H. Whang and A. DasGupta, The Minerals, Metals & Materials Society, Warrendale, PA, 1989, pp. 23-40.

### Awards

IBM Major Outstanding Technical Achievement Award - 2005

IBM Outstanding Technical Achievement Award - 2004

IBM Second Plateau Invention Achievement Award - 1994

IBM First Plateau Invention Achievement Award - 1991

IBM Outstanding Technical Achievement Award - 1989

IBM First Patent Application Award - 1989

Atlantic Richfield Foundation Fellowship (U.C. Berkeley) - 1985

Regent's Fellowship (U.C. Berkeley) - 1984

A.L. Ehrman Memorial Scholarship and S.M. Tasheira Scholarship (U.C. Berkeley) - 1982

Summa Cum Laude (Alfred University, College of Engineering, 1st in class) - 1981

Alcoa Scholarship (Alfred University) - 1981

Refractories Foundation Scholarship (Alfred University) - 1980

Kodak Scholarship (Alfred University) - 1979

Tredennick Scholarship - 1988 through 1981

Pennsylvania State University Scholar (declined) - 1997

National Merit Scholarship Competition finalist -1977

**Professional Organizations and Affiliations**

Chairman, Technical Advisory Board, E2open Corporation

Association of Computing Machinery (ACM)

Institute of Electronics and Electrical Engineers (IEEE)

**BRIEF ATTACHMENT AP**

# RECEIPT

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: April 12, 2006

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

**Mail Stop: AF**

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450



**SECOND AMENDMENT  
AFTER FINAL REJECTION**

Sir:

In response to the Final Office Action dated October 20, 2005 and the Advisory  
Action dated December 28, 2005, please consider the following:

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: April 10, 2006

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

AFFIDAVIT OF DENNIS NEWNS

UNDER 37 C.F.R. 1.132

Sir:

I, Dennis Newns, declare that:

1. I received a B. A. degree in Chemistry form Oxford University United Kingdom in 1964 and a Ph.D. degree in Theoretical Physical Chemistry form the University of London in 1967.

2. I am a theoretical solid state scientist. My resume and curriculum vitae are attached.
3. The USPTO response dated October 20, 2005 at page 4 regarding the subject application cites Schuller et al "A Snapshot View of High Temperature Superconductivity 2002" (report from workshop on High Temperature Superconductivity held April 5-8, 2002 in San Diego) which the examiner states "discusses both the practical applications and theoretical mechanisms relating to superconductivity."
4. The Examiner at page 4 of the Office Action cites page 4 of Schuller et al which states:

"Basic research in high temperature superconductivity, because the complexity of the materials, brings together expertise from materials scientists, physicists and chemists, experimentalists and theorists... It is important to realize that this field is based on complex materials and because of this materials science issues are crucial. Microstructures, crystallinity, phase variations, nonequilibrium phases, and overall structural issues play a crucial role and can strongly affect the physical properties of the materials. Moreover, it seems that to date there are no clear-cut directions for searches for new superconducting phases, as shown by the serendipitous discovery of superconductivity in MgB<sub>2</sub>. Thus studies in which the nature of chemical bonding and how this arises in existing superconductors may prove to be fruitful. Of course, "enlightened" empirical searches either guided by chemical and

materials intuition or systematic searches using well-defined strategies may prove to be fruitful. It is interesting to note that while empirical searches in the oxides gave rise to many superconducting systems, similar (probable?) searches after the discovery of superconductivity in MgB<sub>2</sub> have not uncovered any new superconductors. "

5. The Examiner at pages 4 -5 of the Office Action cites pages 5- 6 of Schuller et al which state:

"The theory of high temperature superconductivity has proven to be elusive to date. This is probably as much caused by the fact that in these complex materials it is very hard to establish uniquely even the experimental phenomenology, as well as by the evolution of many competing models, which seem to address only particular aspects of the problem. The Indian story of the blind men trying to characterize the main properties of an elephant by touching various parts of its body seems to be particularly relevant. It is not even clear whether there is a single theory of superconductivity or whether various mechanisms are possible. Thus it is impossible to summarize, or even give a complete general overview of all theories of superconductivity and because of this, this report will be very limited in its theoretical scope."

6. The Examiner at page 5 of the Office Action cites page 7 of Schuller et al which states:

"Thus far, the existence of, a totally new superconductor has proven impossible to predict from first principles. Therefore their discovery has been based largely on empirical approaches, intuition, and even serendipity. This unpredictability is at the root of the excitement that the condensed matter community displays at the discovery of a new material that is superconducting at high temperature."

7. I am submitting this declaration to clarify what is meant by predictability in theoretical solid state science. All solid state materials, even elemental solids, present theoretical problems. That difficulty begins with the basic mathematical formulation of quantum mechanics and how to take into account all interactions that are involved in atoms having more than one electron and where the interactions between the atoms may be covalent, ionic or Van der Waals interactions. A theory of a solid is based on approximate mathematical formalisms to represent these interactions. A theoretical solid state scientist makes an assessment using physical intuition, mathematical estimation and experimental results as a guide to focus on features of the complex set of interactions that this assessment suggests are dominate in their effect on the physical phenomena for which the theorist is attempting to develop a theory. This process results in what is often referred to as mathematical formalism. This formalism is then applied to specific examples to determine whether the formalism produces computed results that agree with measured experimental results. This process can be considered a "theoretical experiment." For example, applying the theoretical formalism to a particular crystal

structure comprised of a particular set of atoms to compute a value of a desired property is in this context a "theoretical experiment."

8. Even when a successful theoretical formalism is developed, that formalism does not produce a list of materials that have a particular property that is desired. Rather for each material of interest the same "theoretical experiment" must be conducted. Moreover, even if such a "theoretical experiment" indicates that the particular material investigated has the property, there is no assurance that it does without experimentally fabricating the material and experimentally testing whether it has that property.
9. For example, semiconductors have been studied both experimentally and theoretically for more than 50 years. The theory of semiconductors is well understood. A material is a semiconductor when there is a filled valence band that is separated from the next empty or almost empty valence band by an energy that is of the order of the thermal energy of an electron at ambient temperature. The electrical conductivity of the semiconductor is controlled by adding dopants to the semiconductor crystal that either add electrons to the empty valence band or remove electrons from the filled valence band. Notwithstanding this theoretical understanding of the physical phenomena of semiconductivity, that understanding does not permit either a theoretical or experimental solid state scientist to know a *priori* what materials will in fact be a semiconductor. Even with the well developed semiconductor theoretical formalisms, that theory cannot be asked the question "can you list for me all materials that will be a semiconductor?" Just as an experimentalist must do, the theoretical scientist must select a particular material for

examination. If the particular material already exists an experimentalist can test that material for the semiconducting property. If the particular material does not exist, the theoretical solid state scientist must first determine what the crystal structure will be of that material. This in of itself may be a formidable theoretical problem to determine accurately. Once a crystal structure is decided on, the theoretical formalism is applied in a "theoretical experiment" to determine if the material has the arraignment of a fully filled valence and an empty valence band with the correct energy spacing. Such a theoretical experiment generally requires the use of a computer to compute the energy band structure to determine if for the selected composition the correct band configuration is present for the material to be a semiconductor. This must be verified by experiment. Even with the extensive knowledge of semiconducting properties such computations are not 100% accurate and thus theory cannot predict with 100% accuracy what material will be a semiconductor. Experimental confirmation is needed. Moreover, that a theoretical computation is a "theoretical experiment" in the conceptual sense not different than a physical experiment. The theorist starting out on a computation, just as an experimentalist staring out on an experiment, has an intuitive feeling that, but does not know whether, the material studied will in fact be a semiconductor. As stated above solid state scientists, both theoretical and experimental, are initially guided by physical intuition based on prior experimental and theoretical work. Experiment and theory complement each other, at times one is ahead of the other in an understanding of a problem, but which one is ahead changes over time as an understanding of the physical phenomena develops.

10. This description of the semiconductor situation is for illustration of the capability of theory in solid state science where there is a long history of both experimental and theoretical developments.
11. Superconductivity was first discovered by H. Kammerlingh Onnes in 1911 and the basic theory of superconductivity has been known many years before Applicants' discovery. For example, see the book "Theory of Superconductivity", M. von Laue, Academic Press, Inc., 1952 (See Attachment AD of the Third Supplementary Amendment dated March 1, 2005). Prior to applicants' discovery superconductors were grouped into two types: Type I and Type II.
12. The properties of Type I superconductors were modeled successfully by the efforts of John Bardeen, Leon Cooper, and Robert Schrieffer in what is commonly called the BCS theory. A key conceptual element in this theory is the pairing of electrons close to the Fermi level into Cooper pairs through interaction with the crystal lattice. This pairing results from a slight attraction between the electrons related to lattice vibrations; the coupling to the lattice is called a phonon interaction. Pairs of electrons can behave very differently from single electrons which are fermions and must obey the Pauli exclusion principle. The pairs of electrons act more like bosons which can condense into the same energy level. The electron pairs have a slightly lower energy and leave an energy gap above them on the order of .001 eV which inhibits the kind of collision interactions which lead to ordinary resistivity. For temperatures such that the thermal energy is less than the band gap, the material exhibits zero resistivity.

13. There are about thirty pure metals which exhibit zero resistivity at low temperatures and have the property of excluding magnetic fields from the interior of the superconductor (Meissner effect). They are called Type I superconductors. The superconductivity exists only below their critical temperatures and below a critical magnetic field strength. Type I and Type II superconductors (defined below) are well described by the BCS theory.

14. Starting in 1930 with lead-bismuth alloys, a number of alloys were found which exhibited superconductivity; they are called Type II superconductors. They were found to have much higher critical fields and therefore could carry much higher current densities while remaining in the superconducting state.

15. Ceramic materials are expected to be insulators -- certainly not superconductors, but that is just what Georg Bednorz and Alex Muller, the inventors of the patent application under examination, found when they studied the conductivity of a lanthanum-barium-copper oxide ceramic in 1986. Its critical temperature of 30 K was the highest which had been measured to date, but their discovery started a surge of activity which discovered materials exhibiting superconducting behavior in excess of 125 K. The variations on the ceramic materials first reported by Bednorz and Muller which have achieved the superconducting state at much higher temperatures are often just referred to as high temperature superconductors and form a class of their own.

16. It is generally believed by theorists that Cooper pairs result in High T<sub>c</sub> superconductivity. What is not understood is why the Cooper pairs remain together at the higher temperatures. A phonon is a vibration of the atoms about their

equilibrium positions in a crystal. As temperature increases these vibrations are more complex and the amplitude of these vibrations is larger. How the Cooper pairs interact with the phonons at the lower temperature, when these oscillations are less complex and of lower amplitude, is understood, this is the BCS theory. Present theory is not able to take into account the more complex and larger amplitude vibrations that occur at the higher temperatures.

17. The article of Schuller referred to by the Examiner in paragraphs 4, 5 and 6 present essentially the same picture.
18. In paragraph 4 above Schuller states "Of course, 'enlightened' empirical searches either guided by chemical and materials intuition or systematic searches using well-defined strategies may prove to be fruitful. It is interesting to note that while empirical searches in the oxides gave rise to many superconducting systems, similar (probable?) searches after the discovery of superconductivity in MgB<sub>2</sub> have not uncovered any new superconductors." Schuller is acknowledging that experimental researchers using intuition and systematic searches found the other known high Tc superconductors. Systematic searching is applying what is known to the experimental solid state scientist, that is, knowledge of how to fabricate compounds of the same class as the compounds in which Bednorz and Muller first discovered High Tc superconductivity. That a similar use of intuition and systematic searching "after the discovery of superconductivity in MgB<sub>2</sub> have not uncovered any new superconductors" is similar to a "theoretical experiment" that after the computation is done does not show that the material studied has the property being investigated, such as semiconductivity. The Schuller article was published in April 2002

approximately one year after the experimental discovery of superconductivity in MgB<sub>2</sub> was reported on in March 2001 (Reference 8 of the Schuller article. See paragraph 19 of this affidavit.) This limited time of only one year is not sufficient to conclude that systematic searching "after the discovery of superconductivity in MgB<sub>2</sub>" cannot uncover any new superconductors. Experimental investigations of this type are not more unpredictable than theoretical investigations since the experimental investigation has a known blue print or course of actions, just as does a "theoretical experiment." Just as an physical experimental investigation may lead to a null result a "theoretical experiment" may lead to a null result. In the field of High Tc superconductivity physical experiment is as predictable as a well developed theory since the experimental procedures are well known even though very complex. Experimental complexity does not mean the field of High Tc superconductivity is unpredictable since the methods of making these material are so well known.

19. In paragraph 4 above Schuler refers the discovery of MgB<sub>2</sub> citing the paper of Nagamatsu et al. Nature Vol. 410, March 2001 in which the MgB<sub>2</sub> is reported to have a Tc of 39 K, a layered graphite crystal structure and made from powders using know ceramic processing methods. MgB<sub>2</sub> has a substantially simpler structure than the first samples reported on by Bednorz and Muller and therefore can be more readily investigated theoretically. There have been recent reports by Warren Pickett of the University of California at Davis and by Marvin L. Cohen and Steven Louie at the University of California at Berkeley describing progress in a theoretical understanding of the Tc of MgB<sub>2</sub>. It is not surprising that progress in the theory of

superconductivity at 39 K has been made based on this relatively simple material. In fact a few months after the Schuller article was published in April 20002 Marvin .L. Cohen and Steven Louie were authors on an article Choi, HJ; Roundy, D; Sun, H; Cohen, ML; Louie, SG "First-principles calculation of the superconducting transition in MgB<sub>2</sub> within the anisotropic Eliashberg formalism " PHYSICAL REVIEW B; JUL 1, 2002; Vol. 66; p 20513. The following is from the Abstract of this article:

" We present a study of the superconducting transition in MgB<sub>2</sub> using the ab initio pseudopotential density-functional method, a fully anisotropic Eliashberg equation, and a conventional estimate for  $\mu^*$ . Our study shows that the anisotropic Eliashberg equation, constructed with ab initio calculated momentum-dependent electron-phonon interaction and anharmonic phonon frequencies, yields an average electron-phonon coupling constant  $\lambda=0.61$ , a transition temperature Tc=39 K, and a boron isotope-effect exponent  $\alpha(B)=0.32$ . The calculated values for Tc,  $\lambda$ , and  $\alpha(B)$  are in excellent agreement with transport, specific-heat, and isotope-effect measurements, respectively. The individual values of the electron-phonon coupling  $\lambda(k,k')$  on the various pieces of the Fermi surface, however, vary from 0.1 to 2.5. The observed Tc is a result of both the raising effect of anisotropy in the electron-phonon couplings and the lowering effect of anharmonicity in the relevant phonon modes." (Emphasis added)

Thus the statement of the Schuller article in paragraph 5 above "The theory of high temperature superconductivity has proven to be elusive to date" is not totally accurate since shortly after the publication of the Schuller article a theory of the Tc of MgB<sub>2</sub> was published by Marvin .L. Cohen and Steven Louie.

A month later they expanded on this in the article Choi, HJ; Roundy, D; Sun, H; Cohen, ML; Louie, SG "The origin of the anomalous superconducting properties of MgB<sub>2</sub>" NATURE, AUG 15, 2002;Vol 418; pp 758-760. The following is from the Abstract of this article:

" Magnesium diboride ... differs from ordinary metallic superconductors in several important ways, including the failure of conventional models ... to predict accurately its unusually high transition temperature, the effects of isotope substitution on the critical transition temperature, and its

anomalous specific heat .... A detailed examination of the energy associated with the formation of charge-carrying pairs, referred to as the 'superconducting energy gap', should clarify why MgB<sub>2</sub> is different. Some early experimental studies have indicated that MgB<sub>2</sub> has multiple gaps.... Here we report an ab initio calculation of the superconducting gaps in MgB<sub>2</sub> and their effects on measurable quantities. An important feature is that the electronic states dominated by orbitals in the boron plane couple strongly to specific phonon modes, making pair formation favourable. This explains the high transition temperature, the anomalous structure in the specific heat, and the existence of multiple gaps in this material. Our analysis suggests comparable or higher transition temperatures may result in layered materials based on B, C and N with partially filled planar orbitals. (Emphasis added)

Thus the statement in the Schuller article in paragraph 5 above "Thus far, the existence of, a totally new superconductor has proven impossible to predict from first principles" was shown by the work of Marvin .L. Cohen and Steven Louie published shortly after the article of Schuller also to be not totally accurate.

20. In paragraph 5 above Schuller states "The theory of high temperature superconductivity has proven to be elusive to date." As stated above although solid state theorist believe that Cooper Pairs are the mechanism of the High Tc superconductors, we do not as of yet completely understand how to create a mathematical formalism that takes into account the atomic vibrations at these higher temperatures to theoretically permit that electrons to remain paired.

21. In paragraph 5 above Schuller further states "This is probably as much caused by the fact that in these complex materials it is very hard to establish uniquely even the experimental phenomenology." Even though these materials are complex that complexity does not have to be understood to make these material since experimental solid state scientists well understand the method of making these materials. The book "Copper Oxide Superconductors" by Charles P. Poole, Jr.,

Timir Datta and Horacio A. Farach, John Wiley & Sons (1998), [(See Attachment 23 of The Fifth Supplemental Amendment dated March 1, 2004)] referred to herein as Poole 1988 states in Chapter 5 entitled "Preparation and Characterization of Samples" states at page 59:

"Copper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials".

Poole et al. further states at page 61:

"In this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hafsi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor."

22. It is thus clear that experimentalists knew, at the time of Benoraz and Muller's discovery, how to make the High Tc class of material and that to do so it was not necessary to precisely understand the experimental phenomenology.
23. Charles Poole et al. published another book in 1995 entitled "Superconductivity" Academic Press which has a Chapter 7 on "Perovskite and Cuprate Crystallographic Structures". (See Attachment Z of the First Supplementary Amendment dated

March 1, 2005). This book will be referred to as Poole 1995. At page 179 of Poole 1995 states:

"V. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperatute superconductors Bednorz and Müller (1986) referred to their samples as "metallic, oxygen-deficient ... perovskite-like mixed-valence copper compounds." Subsequent work has confirmed that the new superconductors do indeed possess these characteristics."

24. Thus Poole 1988 states that the high  $T_c$  superconducting materials "are not difficult to synthesize" and Poole 1995 states that "the new superconductors do indeed possess [the] characteristics" that Applicants' specification (the patent application currently under examination) describes these new superconductors to have.

25. In paragraph 5 above Schuller states:

"The theory of high temperature superconductivity has proven to be elusive to date. This is ....caused by the fact ... the evolution of many competing models, which seem to address only particular aspects of the problem. The Indian story of the blind men trying to characterize the main properties of an elephant by touching various parts of its body seems to be particularly relevant. It is not even clear whether there is a single theory of superconductivity or whether various mechanisms are possible. Thus it is impossible to summarize, or even give a complete general overview of all theories of superconductivity and because of this, this report will be very limited in its theoretical scope."

The initial development of a theory always considers the problem from many different aspects until the best and most fruitful approach is realized. That at this time "It is not even clear whether there is a single theory of superconductivity or whether various mechanisms are possible" does not mean that experimental solid state scientists do not know how make this class of High Tc materials. As stated by Poole 1988 and Poole 1995 the experimental solid state scientist does know how to make this class of High Tc materials.

26. The Examiner at page 5 of the Office Action cites page 7 of Schuller et al which states:

"Thus far, the existence of, a totally new superconductor has proven impossible to predict from first principles. Therefore their discovery has been based largely on empirical approaches, intuition, and, even serendipity. This unpredictability is at the root of the excitement that the condensed matter community displays at the discovery of a new material that is superconducting at high temperature."

A first principles theory that accurately predicts all physical properties of a material does not exist for as simple a material as water in its solid form as ice which may very well be the most extensively studied solid material. Most theories of solid state materials have phenomenological components that are approximations based on empirical evidence. As stated above solid state theoretical scientists have not as of yet formulated a theoretical formalism that accounts for electrons remaining paired as Cooper pairs at higher temperatures. But this does not prevent experimental scientists from fabricating materials that have structurally similar properties to the

materials first discovered by Bednorz and Muller. This is particularly true since the basic theory of superconductivity were also well known at the time of their discovery and the methods of making these materials was well known at the time of their discovery. It was not necessary at the time of their discovery to have the specific theoretical mechanism worked out in detail in order to make samples to test for High Tc superconductivity. Even Schuller acknowledges "empirical searches in the oxides gave rise to many superconducting systems."

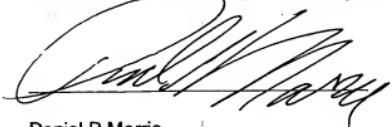
27. I hereby declare that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or patent issued thereon.

Date: 04/11/06

By: D. Newns

Dennis Newns

Sworn to before me this 11<sup>th</sup> day of April \_\_\_\_\_, 2006.



Daniel P Morris

DANIEL P. MORRIS  
NOTARY PUBLIC, State of New York  
No. 4888676  
Qualified In Westchester County  
Commission Expires March 16, 19\_\_\_\_ 2007

## Dr. Dennis M. Newns

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### Professional Preparation and Appointments

1986-Present Physical Science Division, IBM T.J. Watson Laboratory.

1981 Reader, Imperial College London.

1971 Lecturer, Imperial College London.

1969 Postdoctoral Fellow, Department of Physics, Cambridge University.

1967 Postdoctoral Fellow, James Franck Institute, University of Chicago.

1967 Ph.D, Imperial College London.

### Relevant Publications

1. "Polaronic Effects in Mixed and Intermediate Valence Compounds",  
D.M. Newns and A. C. Hewson,  
*J. Phys. C*, 12 1665 (1979).
2. "Mott transition field effect transistor",  
D.M. Newns, J.A. Misewich, and C.C. Tsuei,  
*Appl. Phys. Lett.* 73 780 (1998).
3. "Room-temperature ferromagnetic nanotubes controlled by electron or hole doping",  
L. Krusin-Elbaum, D.M. Newns and H. Zeng,  
*Nature* 431 672 (2004).
4. "Charge-exchange in atom-surface scattering - thermal versus quantum-mechanical non-adiabaticity",  
R. Brako and D.M. Newns,  
*Surf. Sci.* 108 253 (1981).
5. "Desorption induced by multiple electronic-transitions",  
JA Misewich, TF Heinz and D.M. Newns,  
*Phys. Rev. Lett.* 68 3737 (1992).

### Significant Publications

1. "On the solution of the Coqblin-Schrieffer Hamiltonian by the large-N expansion technique", N. Read and D.M. Newns, *J. Phys. C* **16** 3273 (1983).
2. "Anomalous isotope effect and vanhove singularity in superconducting Cu oxides", C.C. Tsuei, D.M. Newns and C.C. Chi, *Phys. Rev. Lett.* **65** 2724-2727 (1990).
3. "Effect of parallel velocity on charge fraction in ion-surface scattering", J. Vanwunnik, R. Brako, K. Makoshi and D.M. Newns, *Surf. Sci.* **12** 618-623 (1983).
4. "Quasi-classical transport at a van hove singularity in cuprate superconductors", D.M. Newns, C.C. Tsuei and R.P. Huebener, *Phys. Rev. Lett.* **73** 1695-1698 (1994).
5. "Self-Consistent Model of Hydrogen Chemisorption" D. Newns, *Phys. Rev.* **178** 1123-1135 (1969).

### Synergistic Activities

1. Work with undergraduate and high school interns as part of the IBM summer research program.
2. Interact with students at APS March meeting lunches.

### Recent Collaborators

W. Donath, M. Shabes, B. Lengfield, M. Eleftheriou, P. Pattnaik, C. Zhou, I. Morgenstern, T. Husslein, P.B. Moore, Q.F. Zhong, L. Krusin-Elbaum, H. Zeng, H.J. Wen, R. Ludeke, T. Doderer, M.L. Klein, J.A. Misewich, C.C. Tsuei, and G.J. Martyna.

### Graduate and Postdoctoral Advisors

Thesis Advisor : E.P. Wohlfarth, Imperial College, London.  
Postdoctoral Advisor : P.W. Anderson, University of Chicago.  
Postdoctoral Advisor : P.W. Anderson, Princeton University.

**BRIEF ATTACHMENT AQ**

# RECEIPT

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: April 12, 2006

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopeck

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

**Mail Stop: AF**

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450



### SECOND AMENDMENT AFTER FINAL REJECTION

Sir:

In response to the Final Office Action dated October 20, 2005 and the Advisory Action dated December 28, 2005, please consider the following:

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
Applicants: Bednorz et al.  
Serial No.: 08/479,810  
Filed: June 7, 1995  
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Date: February 2, 2006  
Docket: YO987-074BZ  
Group Art Unit: 1751  
Examiner: M. Kopec

**DECLARATION OF GEORG BEDNORZ**  
**UNDER 37 C.F.R. 1.132**

Sir:

I, J.Georg Bednorz , declare that:

1. I am a coinventor of the referenced application.
2. I received a M. S. Degree in Mineralogy/Crystallography (1976) from the University of Muenster in Germany and a Ph.D. degree in Natural Science (1982) from the Swiss Federal Institute of Technology (ETH) in Zuerich - Switzerland.
3. The USPTO response dated October 20, 2005 at page 7 cites the following web page <http://www.nobelchannel.com/learningstudio/introduction.sps?id=295&eid=0>

Which states

It is worth noting that there is no accepted theory to explain the high-temperature behavior of this type of compound. The BCS theory, which has proven to be a useful tool in understanding lower-temperature materials, does not adequately explain how the Cooper pairs in the new compounds hold together at such high temperatures. When Bednorz was asked how high-temperature superconductivity works, he replied, "If I could tell you, many of the theorists working on the problem would be very surprised."

4. This declaration is to explain the meaning of the statement attributed to me "If I could tell you, many of the theorists working on the problem would be very surprised" in response to a question from the interviewer about the mechanism of High Tc superconductivity.

5. Following the discovery of the High Tc superconductivity in oxides by my coinventor Alex Mueller and me, the enormous research effort conducted by experimentalist specialized in different disciplines of solid state science created a very complex scenario. After our discovery new layered perovskite-like CuO-compounds with comparable and higher Tc were discovered of the type that are reported on in our original publication and that are described in our patent application. These new materials were made according to known principles of ceramic science that we described in our patent application. The rapid experimental developments were guided by previous work on materials having related the composition and structure. This enormous amount of new information collected over a short period of time made it hard to get a clear picture at that time of the experimental situation for both experimental specialists and theorists. In addition to showing superconductivity at temperatures higher than previously observed, this new information included novel and unusual properties, so far unexplained in the superconducting and normal state. I am an experimental scientist and in the field of solid state science, because of the complexities of theory and experiment, workers in the field are either experimentalist or theorist and typically not both. In this field, including the field of high Tc superconductivity, theory utilizes complex mathematical procedures about which theorists are experts. Thus theorists working in the field would have been surprised if, I, as an experimentalist, had been the sole person in the field to gain a sufficient overview and experimental and theoretical insight, to propose a final theory of high temperature superconductivity at this early stage of research.

6. I hereby declare that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or patent issued thereon.

Date: Feb. 24 /2006

By:

  
J. Georg Bednorz

**BRIEF ATTACHMENT AR**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Date: March 1, 2004

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopc

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 57**

AA



## UNITED STATES DEPARTMENT OF COMMERCE

Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAME INVENTOR	ATTORNEY/DOCKET NO.
07/013,307	05/22/87	HEINRICH?	Y0987-074

EXAMINER  
BUD J

J. DAVID ELLIOTT  
THE INTELLECTUAL PROPERTY LAW FIRM,  
P.O. BOX 218  
YORKTOWN HEIGHTS, NY 10598

ART UNIT  
115

DATE MAILED: 04/25/2024

DUE 7/25/91

This application has been examined  Responsive to communication filed on 2/13/91  This action is made final.

A shortened statutory period for response to this action is set to expire 3 month(s) 0 days from the date of this letter.  
Failure to respond within the period for response will cause the application to become abandoned. 35 U.S.C. 133.

## Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:

1.  Notice of References Cited by Examiner, PTO-892.  
2.  Notice re Patent Drawing, PTO-948.  
3.  Notice of Art Cited by Applicant, PTO-1449.  
4.  Notice of Informal Patent Application, Form PTO-152.  
5.  Information on How to Effect Drawing Changes, PTO-1474.  
6.

## Part II SUMMARY OF ACTION

1.  Claims 1-95 are pending in the application.  
Of the above, claims 12-26, 36-39, 55-59; + 64.. are withdrawn from consideration.  
2.  Claims \_\_\_\_\_ are abandoned.  
3.  Claims \_\_\_\_\_ have been rejected.  
4.  Claims 1-11, 17-35, YU-54, 60-63 + 65 68 are allowed.  
5.  Claims \_\_\_\_\_ are objected to.  
6.  Claims \_\_\_\_\_ are subject to restriction or election requirement.  
7.  This application has been filed with informal drawings under 37 C.F.R. 1.65 which are acceptable for examination purposes.  
8.  Formal drawings are required in response to this Office action.  
9.  The corrected or substitute drawings have been received on \_\_\_\_\_ Under 37 C.F.R. 1.64 these drawings are  acceptable;  not acceptable (see explanation or Notice re Patent Drawing, PTO-948).  
10.  The proposed additional or substitute sheet(s) of drawings, filed on \_\_\_\_\_ has (have) been  approved by the examiner;  disapproved by the examiner (see explanation).  
11.  The proposed drawing correction, filed \_\_\_\_\_ has been  approved;  disapproved (see explanation).  
12.  Acknowledgement is made of the claim for priority under U.S.C. 119. The certified copy has  been received  not been received  been filed in parent application, serial no. \_\_\_\_\_ filed on \_\_\_\_\_  
13.  Since this application appears to be in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.  
14.  Other

1. Applicant's election with traverse of Group I in Paper No. 22 is acknowledged. The traversal is on the ground(s) that the claims of Groups I, II and III are not distinct. This is not found persuasive because the Examiner maintains that the superconductive product, process of making and method of use are directed to potentially distinct inventions. Although there are broad "process" and "method" claims that appear to encompass a great deal of subject matter, the limitations in the dependent claims distinguish the claims of the Groups I, II and III.

The requirement is still deemed proper and is therefore made FINAL.

2. The objection to the specification and objection of claims 1-11, 27-35, 40-54, 60-63 and 65-68 under 35 USC 112, first paragraph, is maintained.

3. The following is a quotation of the first paragraph of 35 U.S.C. § 112:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

4. The Applicants assert that "the scope of the claims as presently worded is reasonable and fully merited" (page 17 of

response). The Examiner disagrees. The present claims are broad enough to include a substantial number of inoperable compositions.

5. The rejection of claims 1-11, 27-35, 40-54, 60-63 and 65-68 under 35 USC 112, second paragraph is maintained.

6. Claims 1-11, 27-35, 40-54, 60-63 and 65-68 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

7. The amended term "rare earth-like" is vague. With respect to the lack of stoichiometry, Applicants argue the superconductive properties can be measured as the composition is varied. This is unpersuasive because the present claims broad enough to require an undue amount of experimentation.

8. The Examiner maintains that the term "doping" is vague. Neither the claim or the specification discuss the limits of the effective amounts of doping.

9. The Applicants assert that a discussion of "electron-phonon interactions to produce superconductivity" is found in the specification. The Examiner maintains that the term is not adequately explained. The specification fails to teach how one determines how to enhance the "electron-phonon" interactions?

10. The term "at least four elements" is indefinite considering the number of elements in the periodic table.

Art Unit 115

11. The rejection of claims 1-11, 27-35, 40-54, 60-63 and 65-68 under 35 USC 102/103 is maintained.

12. Claims 1-11, 27-35, 40-54, 60-63 and 65-68 are rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103 as obvious over each of Shaplygin et.al., Nguyen et.al., Michel et.al. (Mat. Res. Bull. and Revue de Chimie).

13. The Applicants argue that "no prima facie case has been made that the composition anticipates or renders obvious the subject matter" (page 28 of response). The Examiner maintains that these materials appear to be identical to those presently claimed except that the superconductive properties are not disclosed. Applicants have not provided any evidence that the compositions of the cited references are in any way excluded by the language of the present claims, i.e. Applicants have failed to show that these materials are not superconductive. Applicant's composition claims do not appear to exclude these materials.

14. Applicants further argue that under United States patent law they are entitled to claim compositions which might happen to overlap a portion of the concentration ranges broadly recited in the cited references. "The broad statement of a concentration range in the prior art does not necessarily preclude later invention within the concentration range" (page 29 of response). The Examiner fails to understand how Applicant's incredibly broad claims, some of

Art. Unit 115

which require only the presence of a "doped transition metal oxide" (see claim 42), in anyway fall "within" the scope of the compositions disclosed in the prior art. The cited references disclose very specific compositions that not only fall within the scope of the claims, but appear to be identical to those compositions disclosed in the specification as being superconducting. The Examiner maintains that these materials are inherently superconductive and therefore render the claim unpatentable.

15. With respect to Applicants arguments under 35 USC 103 regarding the "question of non-analogous art" and the assertion the cited prior art is irrelevant to the present claim, the Examiner maintains that for the present "composition" claims the references directed to what appear to be identical materials (both in composition and inherent properties) are clearly relevant. The cited individual disclosures appear to be sufficient to maintain the rejection, the Examiner is not relying on any secondary references to modify the teachings in the references.

16. The rejection of claims 1-2, 5-11, 40-44, 46, 48, 51-54, 60, 62 and 66 under 35 USC 102/103 is maintained.

17. Claims 1-2, 5-11, 40-44, 46, 48, 51-54, 60, 62 and 66 are rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103 as obvious over each of Perron-

Art. Unit. 115

Simon et.al., Mossner et.al., Chincholkar et.al., Amad et.al., Blasse et.al., Kurihara et.al. and Anderton et.al.

18. This rejection is maintained for the reasons set forth in the previous paragraphs. The Examiner maintains that the cited references appear to disclose materials which inherently provide superconductive properties and therefore render the present claims unpatentable.

19. THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 C.F.R. § 1.136(a).

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS FINAL ACTION IS SET TO EXPIRE THREE MONTHS FROM THE DATE OF THIS ACTION. IN THE EVENT A FIRST RESPONSE IS FILED WITHIN TWO MONTHS OF THE MAILING DATE OF THIS FINAL ACTION AND THE ADVISORY ACTION IS NOT MAILED UNTIL AFTER THE END OF THE THREE-MONTH SHORTENED STATUTORY PERIOD, THEN THE SHORTENED STATUTORY PERIOD WILL EXPIRE ON THE DATE THE ADVISORY ACTION IS MAILED, AND ANY EXTENSION FEE PURSUANT TO 37 C.F.R. § 1.136(a) WILL BE CALCULATED FROM THE MAILING DATE OF THE ADVISORY ACTION. IN NO EVENT WILL THE STATUTORY PERIOD FOR RESPONSE EXPIRE LATER THAN SIX MONTHS FROM THE DATE OF THIS FINAL ACTION.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to John Boyd whose telephone number is (703) 308-3314.

Any inquiry of a general nature or relating to the status of this application should be directed to the Group receptionist whose telephone number is (703) 308-0661.

Serial No. 07/53,307

-7-

Art. Unit. 115

J. Boyd

April 24, 1991

PAUL LIEBERMAN  
SUPERVISORY PRIMARY EXAMINER  
ART UNIT 115

**BRIEF ATTACHMENT AS**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Date: March 1, 2004

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 39**

# *Inorganic Chemistry*

AN ADVANCED TEXTBOOK

**THERALD MOELLER**

Associate Professor of Chemistry  
University of Illinois

New York · JOHN WILEY & SONS, Inc.  
London · CHAPMAN & HALL, Limited.

Attachment page

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Library of Congress Catalog Card Number: 52-7487

PRINTED IN THE UNITED STATES OF AMERICA

Emphasis up quite generally inorganic chemistry, and, followed by the strongly emphasized recently, inorganic chemistry, rather than up remarkable the and continue position that it

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Attachment A page 2

clathrate compounds). In are crystallized usually those of e at ordinary r components, sent to escape. such the compo-  
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1950); *Research*, 1,

ric compounds as opposed to the normal Daltonide or stoichiometric compounds. As examples, one may cite certain metallic hydrides such as  $\text{VH}_{14}$ ,  $\text{CeH}_{14}$  (p. 411); certain oxides such as  $\text{TiO}_{1.7-1.8}$ ,  $\text{FeO}_{1.04}$ ,  $\text{WO}_{1.32-1.51}$ ; such sulfides, selenides, and tellurides as  $\text{Cu}_1\text{S}$ ,  $\text{Cu}_1\text{Se}$ ,  $\text{Cu}_{1.44}\text{Te}$ ,  $\text{CuFeS}_{1.4}$ ; the tungsten bronzes,  $\text{Na}_x\text{WO}_4$ ; etc. Combinations of these types are particularly common among minerals.

Lack of true stoichiometry of this type is associated with so-called *defect crystal lattices*. Defects in a crystal lattice amount to variations from the regularity which characterizes the material as a whole. They are of two types:

1. *Frenkel defects*, in which certain atoms or ions have migrated to interstitial positions some distance removed from the "holes" which they vacated.

2. *Schottky defects*, in which "holes" are left in random fashion throughout the crystal because of migration of atoms or ions to the surface of the material.

Although both types of defect probably characterize crystals of non-stoichiometric compounds, the Schottky defects are the more important. Obviously detectable departure from true stoichiometric composition can result only if serious defects are present. It would follow, therefore, that many apparently stoichiometric compounds are not truly so. If excess metal is present in a crystal, it may also result from partial reduction of high-valent cations; whereas if excess non-metal is present, higher valent cations or lower valent anions than those normally present may be responsible. Many instances are known of multiple oxidation number in a single crystal. Non-stoichiometric compounds often show semi-conductivity, fluorescence, and centers of color. For a comprehensive discussion of this rather complex subject, a detailed review\*\* should be consulted.

#### SUMMARY OF BOND TYPES

The important linkages which hold together the components of crystalline solids and their general characteristics may be summarized as follows:

1. *Ionic linkages*, in which the crystals are made up of regular geometrical arrangements of positive and negative ions. Such solids tend to possess high melting and boiling points, are hard and difficult to deform, and tend to be soluble in polar solvents. When dissolved in such solvents or fused, they are excellent conductors. Crystals

\*\* J. S. Anderson: *Ann. Reports*, 43, 104 (1946).

Attachment A page 3

overcome. Such cage compounds have been called *cage* or *cage-like* compounds<sup>49</sup> (Latin *cæthratus*, enclosed by cross bars of a grating). In general, they occur when mixtures of the components are crystallized under optimum conditions. Their properties are roughly those of the enclosing material. Such compounds are stable at ordinary temperatures with respect to decomposition into their components, but melting or dissolution permits the enclosed component to escape. Examples are hydroquinone compounds which approach the composition  $(C_6H_4O_2)_n \cdot X$  ( $X = HCl, HBr, H_2S, CH_3OH, SO_2, CO_2, HCN$ , etc.); amine compounds containing sulfuric acid, e.g.,  $(p\text{-H}_2NC_6H_4NH_3^+)_n \cdot H_2SO_4$ ; phenol compounds, e.g.,  $(C_6H_5O_2)_n \cdot SO_2, (C_6H_5O_2)_n \cdot CO_2$ ; and certain compounds of the inert gas elements (pp. 382-383).

It is obvious that the conditions under which clathrate compounds can form are limited and highly specific. Among those of importance are:

1. An open crystal structure in the enclosing component. This necessitates directed linkages holding the molecule and crystal together, sufficient extension of the groups to form a cavity of suitable size, and a rigid structure.
2. Small access holes to the enclosed cavity. This may result from either proper disposition of groups in the formation of the crystal or sufficient surface area in the enclosing groups.
3. Ready availability of the trapped component at the time when the cavity is closed.

Such compounds are of considerable theoretical interest but are lacking in practical importance. Information on possible arrangements in clathrate compounds and the structures which lead to them is to be found in Powell's discussions.<sup>22</sup>

## NON-STOICHIOMETRIC COMPOUNDS

The law of definite proportions is one of the basic tenets of chemistry. Its validity is indicated by the restrictions imposed upon bond formation where electrons are involved as already outlined, and its application is generally the assumed basis for any type of chemical combination. There are, however, many instances of apparent departure from this rule among solid compounds. Such compounds do not possess exact compositions which are predicted from electronic considerations alone and are commonly referred to as Berthollide or non-stoichiometric.

<sup>\*\*</sup> H. M. Powell: *J. Chem. Soc.*, 1948, 61; *Endeavour*, 9, 154 (1950); *Research* 353 (1947-1948).

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Attachment A page 4

*Fundamentals  
of  
chemistry  
a  
modern  
introduction*

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**FRANK BRESCIA**

**JOHN ARENTS**

**HERBERT MEISLICH**

**AMOS TURK**

*Department of Chemistry  
The City College of the  
City University of New York*



**ACADEMIC PRESS**

*New York and London*

*Attachment A page 5*

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Second Printing, April, 1966

PRINTED IN THE UNITED STATES OF AMERICA

Attachment A page 6

*matter: the mass of a chemically reacting system remains constant.* This law is consistent with the data obtained with the most precise balances available. If matter is created or destroyed, the quantity is less than can be detected with the best available balance.

#### 4.2 THE LAW OF DEFINITE PROPORTIONS

Analyses of compounds show that when elements form a given compound, they always combine in the same ratio by weight. For example, independently of the source or method of formation, silicon dioxide,  $\text{SiO}_2$ , contains 46.7% by weight of silicon and 53.3% of oxygen. This knowledge is summarized in the *law of definite proportions: the weight composition of a given compound is constant.*

**EXAMPLE 1** 10.0 g of silicon dust, Si, is exploded with 100.0 g of oxygen,  $\text{O}_2$ , forming silicon dioxide,  $\text{SiO}_2$ . How many grams of  $\text{SiO}_2$  are formed and how many grams of  $\text{O}_2$  remain uncombined?

**ANSWER** Since 46.7 g of Si combines with 53.3 g of  $\text{O}_2$ , the quantity of  $\text{O}_2$  required per gram of Si is

$$\frac{53.3 \text{ g O}_2}{46.7 \text{ g Si}}$$

and, therefore, for 10.0 g of Si, the quantity of  $\text{O}_2$  required is

$$\frac{53.3 \text{ g O}_2}{46.7 \text{ g Si}} \times 10.0 \text{ g Si} = 11.4 \text{ g O}_2$$

Hence, the weight of  $\text{SiO}_2$  formed is  $10.0 \text{ g} + 11.4 \text{ g} = 21.4 \text{ g}$  and the weight of uncombined  $\text{O}_2$  is  $100.0 \text{ g} - 11.4 \text{ g} = 88.6 \text{ g}$ .

#### 4.3 THE ATOMIC THEORY

The weight relationships of substances participating in chemical reactions are clearly explained in terms of the atomic theory. Although John Dalton (1803) is generally recognized as the inventor of the theory, he was anticipated by other scientists, particularly William Higgins (1789). Thus, it appears that the law of multiple proportions (Section 4.4) was foreshadowed by Higgins and Dalton from their respective atomic theories. A verified prediction made by a theory constitutes the strongest argument in its favor. However, the novel and central point of Dalton's activities was the attempt to determine the relative weights of atoms. This goal focused attention upon the theory, and revealed a new field of human endeavor that ultimately made chemistry a systematized body of knowledge.

The assumptions of the atomic theory were

- (i) *The elements are composed of indivisible particles called atoms.*
- (ii) *All the atoms of a given element possess identical properties, for example, mass.*

**BRIEF ATTACHMENT AT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Date: March 1, 2004

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

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**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

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AT

# THEORY OF SUPERCONDUCTIVITY

By

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SYMBOLS	
$A$	vector potential
$a_p$	undetermined constants, $\phi = 1, 2, \dots$
	a numerical ratio
$a_p$	undetermined constants, $\phi = 1, 2, \dots$
$B$	magnetic induction
$d$	reciprocal penetration depth
$c$	velocity of light
$C_m$	closed curves $m = 1, 2, \dots$
$x$	specific heats per mol of normal and superconducting phases an undetermined multiplier
$D$	electric displacement
$d$	distance
$dA$	work done in virtual displacement
$dA$	work done in material displacement
$dF$	change in free energy in virtual displacement
$dn$	virtual displacement of a surface element
$ds$	surface element
$ds$	line element
$d\tau$	volume element
$du$	material displacement
$dV$	potential energy change due to material displacement
$E$	electric field intensity
$E_0$	electric field components, $\alpha = 1, 2, 3$
$E$	total energy
$E_0$	amplitude of $E$ waves
$[E \times H]$	vector product of $E$ and $H$
$\epsilon$	dielectric constant
$F$	free energy
$f_{RN}$	free energy per mol of normal and superconducting phases
$F_n$	force per unit area due to Maxwell stresses
$F^2$	free energy of supercurrent
$G$	electromagnetic momentum associated with the supercurrent
$Q_a$	components of $G$ , $\alpha = 1, 2, 3$
$\gamma$	a numerical factor
$H$	magnetic field intensity vector
	components of $H$ , $\alpha = 1, 2, 3$
$H^0$	external homogeneous magnetic field
$H_e$	critical magnetic field
$H_i$	internal and external values of $H$
$H_0(x)$	Hankel's function of $x$ , first kind zero order
$H_1(x)$	Hankel's function of $x$ , first kind first order
$I$	electric current in a line or current in a surface
$I$	electric current density vector
$I_a$	components of $I$ , $\alpha = 1, 2, 3$
$I_b$	$I_b$ , $I_b$ components of $I$ , cartesian or polar
$I_c$	ohmic current density vector
$I_p$	supercurrent density vector
$I_m$	maximum current density vector
$I_n$	current density normal to a given surface element
$I_s$	scalar density of current
$I^2$	scalar product of $I$ and $G$
$I_n(x)$	square root of $I_m$ minus one
$K$	Bessel functions, $n = 0, 1, 2, \dots$
$k_n$	complex wave number
$K_n$	complex wave number for normal conductor
$K$	total force on a surface element due to electromagnetic stress
$K$	force per unit volume in matter due to Maxwell-London stresses
$L$	a length
$\lambda$	superconductivity constant
$\lambda_{ab}$	superconductivity tensor $a, \beta = 1, 2, 3$
$M$	intensity of permanent magnetisation
$\mu$	magnetic permeability
$N$	number of superconducting electrons per cubic centimeter
$n$	unit normal vector
$n_o, n_s$	unit normal vector directed inwards or outwards
$\nu$	frequency (numerical)
$P_n$	force on surface due to London stresses
$\phi_{RN}$	coefficients of induction $a, \beta = 1, 2, \dots$
$\phi_{RN}$	self-induction for superconductors
$p_R$	mutual induction between super- and normal conductor
$\varphi$	azimuthal angle
$\Phi$	imaginary part of a complex function
$\Phi$	electrostatic or magnetostatic potential
$\Psi$	real part of a complex function
$Q$	superconduction scalar potential
$Q$	quantity of heat
$Q$	cross cut in $n$ -ply connected region
$Q$	rate of flow of energy in radiation field

$R$  real part of complex function  
 $R$  a radius  
 $R_i, R_o$  internal and external radii  
 $r, \theta, \varphi$  polar coordinates  
 $\rho$  charge density  
 $\rho^0$  charge density for ohmic current carriers  
 $\rho'$  charge density for supercurrent carriers  
 $s_1, s_2$  entropy per mol in normal and superconducting phases  
 $S_c$  linear dimensions of a multiple valued function on a curve  $C$   
 "period" of a multiple valued function on a curve  $C$   
 $\sigma$  electric conductivity tensor  
 $\sigma_{ab}$  electric conductivity tensor  $a, b = 1, 2, 3$   
 $T$  temperature in  $^{\circ}\text{K}$   
 $T_c$  transition temperature for superconductivity  
 $T(B)$  Maxwell stress tensor  
 $T(H)$  Maxwell stress tensor  
 $t_a$  time  
 $t_e$  numerical constants  $a = 1, 2, \dots$   
 $\theta$  latitude angle  
 $\theta_1, \theta_2$  Debye temperatures for normal and superconducting phases  
 $\theta_{ab}$  The London stress tensor in superconductor  $a, b = 1, 2, 3$   
 $U$  total energy of the field  
 $U$  real part of complex function  $W$   
 $u$  a general function of position and time  
 $V$  volume or potential  
 $V$  imaginary part of complex function  $W$   
 $W$  electromotive force  
 $W$  resistance  
 $\omega$  angular frequency  
 $\mathcal{W}(\cdot)$  differential operator for the telegrapher's equation  
 $x, y, z$  cartesian coordinates  
 $x_1, x_2, x_3$  cartesian coordinates  
 $\chi$  permeability  
 $\chi$  a function in the complex plane  
 $Z$  complex impedance  
 $\zeta$  a function in the complex plane  
 $\zeta$  a variable of integration

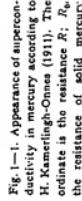
## CHAPTER I

## Fundamental Facts

(a) Superconductivity was discovered in 1911 by Kamerlingh-Onnes.<sup>1</sup> He was the first to liquefy helium and so to produce temperatures below  $10^{\circ}\text{K}$ . With this new technique he was able to observe the continued decrease of the electrical resistance of metals with decreasing temperature. With mercury, in contrast to other metals, he was astonished to find that the resistance completely vanished, almost discontinuously, at about  $4.2^{\circ}\text{K}$  (Fig. 1-1). Today superconductivity is known in 18 other metals (see Table 1-1) whereas in others, e. g., gold and bismuth, the conductivity remains normal even  $1^{\circ}\text{K}$ . Many alloys and compounds can also become superconducting; in particular the frequently used niobium nitride which has a transition temperature as high as  $20^{\circ}\text{K}$ . However, among these latter substances hysteresis phenomena mentioned in the "Introduction" are so much more strongly evident that in testing the present theory we prefer to employ only the "good" superconductors, i. e., the pure elements.

In the ideal case the resistance vanishes completely and discontinuously at the transition temperature  $T_c$ . Actually the resistance-temperature curve does fall more sharply than the more the specimen is like a single crystal and the smaller the measuring current used. Because the drop always occurs in a measurable temperature range, the experimental definition of the transition temperature is to some extent arbitrary. The temperature at which the direct-current resistance reaches one half of the value it had just before the drop is generally given as the transition temperature, because this can be measured accurately. However, a high-frequency investigation to be described in Chap. 16 (f) indicates that the foot of the curve where

Fig. 1-1. A appearance of superconductivity in mercury according to H. Kamerlingh-Onnes (1911).

<sup>1</sup>H. Kamerlingh-Onnes, *Commun. Leiden*, 120th, 124e. (1911).

the d-c resistance becomes unmeasurably small represents the true transition point, because of this uncertainty Table I-1 quotes the transition points only to one-tenth of a degree.

Table I-1

Superconducting Elements

Name	Atomic Number	Transition Temperature	Cryostatographic System	Crystal Class*
Aluminum	13	1.2 °K	Cubic	O <sub>h</sub>
Titanium	22	0.5 °K	Cubic and hexagonal	O <sub>h</sub> and D <sub>4h</sub>
Vanadium	23	4.3 °K	Cubic	O <sub>h</sub>
Zinc	30	0.9 °K	Hexagonal	D <sub>3h</sub>
Gallium	31	1.1 °K	Rhombohedral	V <sub>4h</sub>
Zirconium	40	0.7 °K	Cubic and hexagonal	O <sub>h</sub> and D <sub>4h</sub>
Niobium	41	9.2 °K	Cubic	O <sub>h</sub>
Cadmium	48	0.6 °K	Hexagonal	D <sub>3h</sub>
Indium	49	3.4 °K	Tetragonal†	D <sub>4h</sub>
Tin	50	3.7 °K	Tetragonal†	D <sub>4h</sub>
Lanthanum	57	4.7 °K	Cubic and hexagonal	O <sub>h</sub> and D <sub>4h</sub>
Hafnium	72	0.3 °K	Hexagonal	D <sub>4h</sub>
Tantalum	73	4.4 °K	Cubic	O <sub>h</sub>
Rhenium	76	0.9 °K	Hexagonal	D <sub>3h</sub>
Mercury	80	4.2 °K	Rhombohedral	D <sub>3d</sub>
Thorium	81	2.4 °K	Cubic and hexagonal	O <sub>h</sub> and D <sub>4h</sub>
Lead	82	1.2 °K	Cubic	O <sub>h</sub>
Thorium	90	1.4 °K	Cubic	O <sub>h</sub>
Uranium	92	0.8 °K	Rhombohedral	V <sub>4h</sub>

\* The atomic structures does not change during the transition from normal conductor to superconductor; therefore the crystal class does not change either. The classes are defined according to diamond type pitch, however, does not become superconducting with a crystal structure of the diamond type pitch.

† Besides the tetragonal there exists a gray modification with a crystal structure of the orthorhombic type which, however, does not become superconducting.

In order to obtain curves such as in Fig. 1-1, the resistance is calculated from the potential drop along a wire carrying a current. For this purpose the leads are soldered to the ends of the wire, in addition to the leads for the current, and are connected to a highly sensitive potentiometer. But if one merely wishes to verify the complete disappearance of the resistance below the transition temperature  $T_c$ , experiments with persistent currents, also due to Kamerlingh-Onnes,<sup>2</sup> are far more exact.

(b) One possible procedure is to place ring or short-circuited coil in a magnetic field while its temperature is still above  $T_c$ , cool it down until superconductivity appears, and then remove it from the field. The induced

<sup>2</sup> H. Kamerlingh-Onnes, *Commun. Leiden*, 140b, 141b, (1914).

## 1. FUNDAMENTAL FACTS

electromotive force produces a current in the superconductor which will persist indefinitely unchanged in magnitude as long as superconductivity remains. The ring forms an ideal permanent magnet, and, when placed in an external homogeneous magnetic field, it experiences a torque corresponding to its magnetic moment. Two rings with persistent currents attract or repel each other, depending on their relative orientations, just as for ordinary currents, except that no emf's are needed to maintain them. It does not matter whether the rings are homogeneous or consist of several different superconductors, or whether their temperature is constant in space or time; it is only necessary that no part of the ring shall leave the superconducting state. Should this occur, the current is quenched almost instantaneously. For example, a ring carrying a persistent current may be cut at some point across which a galvanometer has been connected through normally conducting leads. Before the cut is made, the galvanometer will register zero current; but at the instant that the ring is broken, it will show a short current impulse. The energy of the persistent current, for the most part magnetic energy, is then transformed into Joule heat in the normally conducting wires.

A necessary condition for the existence of any persistent current is that the superconductor form a doubly connected body or, briefly, a ring, or more generally a multiply connected body. No persistent currents can exist in a simply connected body such as a sphere. Results that apparently contradict this arise because only parts of the specimen among them doubly or multiply connected parts, may become superconducting, while the rest of the specimen remains either normal or in the intermediate state (see Chap. 12 (§) and 19). An electromagnet using the persistent current has been described by E. Justi.<sup>3</sup>

(c) In contrast to the normal current, which we shall call the ohmic current, the superconducting current (or supercurrent) does not penetrate very far into the specimen. It has been known for a long time that the superconductivity of thin tin films on copper or some other normally conducting metal, even down to a thickness of only  $10^{-4}$  cm does not differ from the superconductivity of thick tin wires. The contradictory evidence found by Burton<sup>4</sup> using somewhat thinner films is outweighed by the observations of Shashik<sup>5</sup> and by those of Appleyard and Misener<sup>6</sup> using lead, tin, and mercury films as thin as  $5 \times 10^{-5}$  cm. These workers found practically the same transition temperatures as in the bulk metals, the small differences observed being within the experimental error.

The first quantitative estimates of the penetration depth of the supercurrent and its associated magnetic field derived from observational evidence,

<sup>3</sup> It is fairly certain that temperature fluctuations have no effect because no investigator has ever mentioned any such effect.

<sup>4</sup> E. Justi, *Fizika*, 2, 48, 57 (1942).

<sup>5</sup> E. F. Burton, *Nature*, 188, 459 (1941).

<sup>6</sup> A. Shashik, *Nature*, 148, 74 (1950).

<sup>7</sup> T. S. Appleby and A. D. Misener, *Nature*, 149, 474 (1938).

were made by the author<sup>4</sup> from the experimental results of Pontius using lead wires<sup>5</sup> [Fig. 18-1]. Applebyard, Bristow, and H. London<sup>6</sup> and a year later Shoenberg<sup>7</sup> found the same order of magnitude, namely  $10^{-4}$  cm. using films and spherical drops of mercury. This holds for temperatures within a few tenths of a degree below the transition temperature  $T_c$ . However, if we are within one-tenth of a degree of  $T_c$ , according to the above work of Shoenberg, the penetration depth increases suddenly and appears to become infinitely great at the transition point (see Fig. 11-3). This means that in a certain sense the electrical properties of the superconductor change continuously into those of the normal conductor. The measurements by McLeanian, Burton, Pitt and Wilhelm<sup>8</sup> and H. London<sup>9</sup> on the high-frequency resistance of superconductors also fit in with this concept: the resistance to rapid oscillations showed no discontinuity at the transition point, but joined smoothly at  $T_c$  with that of the high-frequency resistance of the normal conductor (Fig. 16-2).

(d) The transition from normal to superconductor does not change the form or the volume of the specimen; its lattice remains the same not only in its symmetry but also in its three lattice constants. This was proved by lead by Kamerlingh-Onnes and Keesom using x-ray analysis.<sup>10</sup> The coefficient of thermal expansion (which incidentally is very small) does not change at the transition. Of special significance is the optical identity of the two phases, because in normal conductors the optical constants are intimately related to the electrical conductivity. The observations of Dautt, Keddy, and Mendiss<sup>11</sup> of Hirschlaff<sup>12</sup> and of Hilsch<sup>13</sup> revealed no difference in the electrical conductivity. The observations of Dautt, difference in the appearance of the metal. One cannot tell by visual observation whether the metal is normal or superconducting.

(e) The relation between superconductivity and magnetic field is of the highest significance. The first steps toward disclosing this relation were made in 1913 by Kamerlingh-Onnes<sup>14</sup> who noticed that at each temperature there existed a critical value  $H_c$  of the magnetic field that would destroy the superconductivity. We can obtain the simplest and clearest results by putting a wire in a longitudinal magnetic field, i. e.,

<sup>4</sup>M. V. Laue, *Ann. Physik*, **92**, 71, 255 (1937).

<sup>5</sup>R. B. Pontius, *Nature*, **146**, 1055 (1939).

<sup>6</sup>T. S. Applebyard, T. R. Bristow, and H. London, *Nature*, **148**, 435 (1939).

<sup>7</sup>D. Shoenberg, *Nature*, **148**, 434 (1939).

<sup>8</sup>E. Laumann and D. Shoenberg, *Nature*, **160**, 747 (1948).

<sup>9</sup>C. McLeanian, A. C. Burton, A. Pitt, and J. O. Wilhelm, *Proc. Roy. Soc. (London)*, **186**, 52 (1932); **188**, 245 (1934).

<sup>10</sup>H. London, *Proc. Roy. Soc. (London)*, **176**, 522 (1940).

<sup>11</sup>J. G. Dautt, T. C. Keey, and K. Mendisschow, *Commun. Leiden*, **174b** (1924).

<sup>12</sup>W. H. Keesom and H. Kamerlingh-Onnes, *Commun. Leiden*, **174b** (1924).

<sup>13</sup>E. Hirschlaff, *Proc. Cambr. Phil. Soc.*, **38**, 264 (1937).

<sup>14</sup>R. Hilsch, *Physik Z.*, **40**, 592 (1939).

<sup>15</sup>H. Kamerlingh-Onnes, *Commun. Leiden Supplenumen*, **85** (1913).

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parallel to the axis of the wire. The dependence of the a-c-resistance on the magnetic field  $H$  for this case is shown in Fig. 1-2, while Fig. 1-3 shows the critical value of the magnetic field as a function of temperature for several metals.

Figure 1-4 shows an extrapolation of these curves down to the absolute zero of temperature according to a relation that is empirically confirmed in some cases:

$$H_c = a(T_c - T)$$

At  $T = 0$  the tangent of this curve is horizontal, as thermodynamics demands (Chap. 17). The maximum values of  $H_c$  at  $T = 0$  lie between 100 and 1000 oersteds for pure metals and may be much higher for alloys and compounds.

Fig. 1-2. Transition to superconductivity in a longitudinal magnetic field for tin at different temperatures. (After Steiner and Grässmann, *Supralitungen*, Braunschweig, 1935.)

Fig. 1-3. Critical value of the magnetic field  $H_c$  as a function of temperature for different metals. (After Steiner and Grässmann, *Supralitungen*, Braunschweig, 1935.)

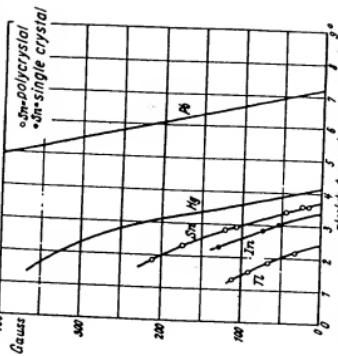
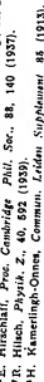


Fig. 1-3. Critical value of the magnetic field  $H_c$  as a function of temperature for different metals. (After Steiner and Grässmann, *Supralitungen*, Braunschweig, 1935.)



A current  $I$  produces at the surface of a straight wire of radius  $R$  a magnetic field  $H$ :

$$H = \frac{I}{2\pi R} \quad (1-1)$$

In Lorentz units, which we shall generally employ,<sup>18</sup> we should therefore expect to find a critical value  $I_c$  of the current which would destroy superconductivity, and this has been confirmed by observation. According to eq. (1-1) the relation between  $I_c$  and  $H_c$  ought to be

$$I_c = 2\pi c R H_c \quad (1-2)$$

This was first pointed out by Shibaev,<sup>19</sup> and it is therefore called the Shibaev hypothesis. Most measurements do not agree with eq. (1-2), although in one case it has been confirmed by a very careful series of measurements by Shibaev and Alekseev.<sup>20</sup> This is one of the weakest points in our understanding of superconductivity; a failure of eq. (1-2) means nothing less than a failure of the fundamental Maxwell relation connecting curl  $\mathbf{H}$  and current density  $I$ . No one at present credits such a failure, and the theory developed here is based soon able to remove this uncertainty.

(f) The earliest theory of superconductivity visualized the superconductor as simply a conductor with zero resistance. But on the Maxwell theory this assumption would have an important consequence, the interior of a perfect conductor would be completely shorted off electromagnetically from any outside influence. If such a conductor were placed in a static magnetic induction, its interior would remain field free, the lines of force, or rather of a body, would diverge in front and converge behind as if going round were one to put the specimen in an external field while it was still above the transition temperature  $T_c$ , and then cool it in the field until the resistance disappeared. Above  $T_c$  the lines of force would go through the metal without difficulty because the permeability  $\mu$  of the metals under consideration is practically unity so long as they are in the normal state. This theory however asserts that the appearance of superconductivity cannot by itself alter the field. The lines of force would still go through the specimen undivided. On the contrary, Meissner and Ochsenfeld<sup>21</sup> showed in 1933 that the final

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state is in fact identical in the two cases — it does not depend on the previous history. In a single connected superconductor everything is uniquely determined by its temperature and the apparatus producing the external field: in an n-ply connected body there is a possibility of n — persistent currents and their magnetic fields whose strengths are optional within certain limits. But in any case the interior of a sufficiently thick superconductor is field free. The field-free state is the only state in such a superconductor.

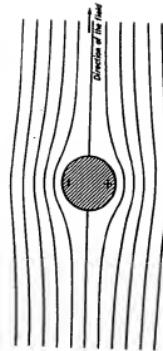


Fig. 1-4. Critical value of the magnetic field  $H_c$  as a function of temperature for lead (approximate curve).

difficulty because the permeability  $\mu$  of the metals under consideration is practically unity so long as they are in the normal state. This theory however asserts that the appearance of superconductivity cannot by itself alter the field. The lines of force would still go through the specimen undivided. On the contrary, Meissner and Ochsenfeld<sup>21</sup> showed in 1933 that the final

<sup>18</sup> If  $I$  is measured in amperes and  $H$  in oersteds,  $H = 0.2 I/R$ .

<sup>19</sup> F. B. Shibaev, *J. Washington Acad. Sci.*, 6, 597 (1916).

<sup>20</sup> L. W. Shubnikov and N. E. Alekseev, *Nature*, 188, 804 (1956).

<sup>21</sup> W. Meissner, and R. Ochsenfeld, *Naturwissenschaften*, 21, 787 (1933).

Fig. 1-5. The transverse field near a superconducting circular cylinder. The lines  $(r - R(r)) \sin \theta = C$  for  $C = 0, \pm 1/2 R, \pm R, \pm 3R/2, \pm 2R, \pm 5R/2$ , + or — means the supercurrent flows toward or away from the reader respectively.

This fact permits us to interpret the super- and normal conductors as two phases of the same substance, whereas according to the older theory the state inside the superconductor was not determined intrinsically. Under this condition we can now apply thermodynamics to the equilibrium between the normal and the superconducting state (see Chap. 17). The London extension of the Maxwell theory is also based essentially on the expansion of the field, called the Meissner effect.

(g) The older conception permitted us to calculate the field deformation near a thick superconductor accurately enough when the cooling precedes the application of the field. It showed that the distortion of the lines of force at certain points of the surface increases the field strength (see Fig. 1-5); for a superconducting sphere in a homogeneous field by a maximum factor 3/2; for a circular cylinder in a transverse field by a factor 2, and for an elliptical cylinder with cross-sectional axes  $a$  and  $b$  by the factor  $(1 + b/a)$  when the field is parallel to the  $a$  axis.

It was thus possible in 1932 — even before the Meissner discovery — for the author<sup>22</sup> to explain the fact that a transverse external field  $H_x$  was sufficient to quench the superconductivity in a wire. It was also predicted that an elliptical cylinder would show a greater decrease of the apparent

<sup>22</sup> M. v. Laue, *Physik*, 2, 88, 793 (1932).

critical value than a circular cylinder if the field were perpendicular to the greater axis; also for a square the apparent critical value would amount to  $(2/5)H_c$  (see Chap. 10 (e) and (d), and Chap. 11). All these predictions were confirmed by an extensive series of measurements by de Haas and co-workers<sup>11</sup> et al.<sup>12</sup>. In this work it was also found that there must certain indication of the breakdown of superconductivity if there is not certain of an ohmic resistance, but the appearance of a magnetic field in the interior of the specimen as detected by means of small bi-spiral wires placed in cavities in the specimen. The whole specimen does not immediately become the "intermediate state" with the disappearance of superconductivity; instead normal and superconducting parts (Chap. 19). As long as the latter form connected paths they take over the conduction of the current exclusively.

(A) Finally our book will discuss thermal measurements, e. g., the heat that takes place in a magnetic field, or the specific heats of the normal and superconductors. But we shall postpone any more detailed discussion of this until Chap. 17 where the thermodynamics will reveal relations between these caloric phenomena and the critical magnetic field.

## CHAPTER 2

**Current Distribution Between Superconductors in Parallel**  
(e) If between two points of a normally conducting system there are  $n$  branches with resistances  $r_1, r_2, \dots, r_n$ , then the ratios of the direct currents

$$I_1 : I_2 : \dots : I_n = \frac{1}{r_1} : \frac{1}{r_2} : \dots : \frac{1}{r_n}$$

This rule of Kirchhoff's remains valid when one branch becomes superconductor short-circuits all the other branches. If we apply an emf to such a system consisting of all the same metal above the transition temperature, then the rule still holds even if we cool the metal until superconductivity appears. The appearance of superconductivity does not change the individual currents if the total current  $\sum_{k=1}^n I_k$  is kept constant.

As a matter of fact any (possible) cause for such a change disappears as the mutual inductions between all the currents  $I_k$  vanish.

<sup>11</sup>W. J. de Haas and J. M. Casimir-Jonker, *Physica*, 1, 291 (1934).

<sup>12</sup>W. J. de Haas and O. A. Guinier, *Physica*, 1, 297 (1934).

<sup>13</sup>W. J. de Haas, A. J. Fengeles, and O. A. Guinier, *Physica*, 4, 595 (1937).

## 2. CURRENT DISTRIBUTION — PARALLEL SUPERCONDUCTORS

If initially all values of  $r_i = 0$ , the Kirchhoff rule cannot be applied at all. The calculation of the current distribution must be based upon the fact that the current is initiated by means of a voltage  $V$ , formed between the junctions, which changes with time and dies out as soon as the currents become stationary, the whole process being described in terms of the laws of induction. In using these laws we have to assume that the inductive coupling between the  $n$  branches is much stronger than their coupling with the leads to the junctions. This condition is fulfilled by inserting coils with considerable mutual inductance in the branches and by having the leads in the form of straight wires which do not come too close to the coils. The magnetic field of the system is then mainly confined to the vicinity of the coils.

Under these conditions the magnetic field strength  $H$  is a linear function of the currents  $I_k$  at every point; the energy density  $V_2/4\pi$  and also the total magnetic energy

$$\frac{1}{2} \int H^2 ds dy dz = \frac{1}{2} \sum_{k=1}^n \rho_{ik} I_k I_i$$

is therefore a quadratic form in  $I_k$ . This form is necessarily positive and definite, i.e., all  $\rho_{ik}$  the determinant of the  $\rho_{ik}$  as well as all subdeterminants symmetrical with respect to the diagonal, are positive. For  $n = 2$ ,

$$\rho_{11} > 0, \quad \rho_{22} > 0, \quad \rho_{11}\rho_{22} - \rho_{12}^2 > 0 \quad (2-1)$$

The  $\rho_{ik}$  are the coefficients of self induction, the "mixed" terms  $\rho_{ik}$  are the coefficients of mutual induction,  $\rho_{kk} = \rho_{kk}$  identically. It is possible to derive Maxwell's equations from the principle of least action by considering the electric energy as the potential energy and the magnetic energy as the kinetic energy. If electric currents are flowing, the work  $V$  performed by the current's has to be taken into consideration, where  $d\theta$  is the amount of electricity transported in a given direction by the current  $I$ . Here we have to do with quasi-stationary processes for which the electric energy vanishes compared with the magnetic energy. Under the assumption that the magnetic energy is the only energy depending on the currents, this principle now reads:

$$\delta \int \left( \frac{1}{2} \sum_{k=1}^n \rho_{ik} I_k I_i - V \sum_{k=1}^n \epsilon_k \right) dt = 0 \quad (2-2)$$

As  $-I_k = da_k/dt$  is the velocity corresponding to the coordinate  $a_k$ , the corresponding Euler equations are

$$\frac{d}{dt} \left( \sum_{k=1}^n \rho_{ik} I_k \right) - V = 0 \quad (k = 1, 2, \dots, n) \quad (2-3)$$

and we recognize these as the usual induction equations. They are immediately integrable with respect to time  $t$ , and if all  $I_k$  are zero at  $t = 0$  we obtain

$$\sum_i \rho_{ii} I_i = \int V dt \quad (2-4)$$

This holds for all times, including the final state in which all  $I_i$  have become stationary and  $V = 0$  by eq. (2-3). Unfortunately the quantity  $\int V dt$  is not determined by the experiment, but only the current  $I = \sum_i I_i$  in the steady state namely by a galvanometer in the leads. However, together with the equation  $I = \sum_i I_i$ , eq. 2-4 forms  $n+1$  linear relations between the  $n+1$  unknowns  $I_1, I_2, \dots, I_n$  and  $V dt$ . For the special case  $n=2$ , eq. 2-4 gives

$$\rho_{11} I_1 + \rho_{12} I_2 = \rho_{21} I_1 + \rho_{22} I_2 = \int V dt \quad (2-5)$$

Therefore because  $I_1 + I_2 = I$  we have

$$I_1 = \frac{\rho_{22} - \rho_{12}}{\rho_{11} + \rho_{12} + 2\rho_{21}} I \quad I_2 = \frac{\rho_{11} - \rho_{21}}{\rho_{11} + \rho_{12} - 2\rho_{21}} I \quad (2-6)$$

We regard  $I$  as positive; a positive  $I_1$  means that this current flows in the same direction as  $I$ ; a negative  $I_1$  means that it has the opposite direction. According to eq. 2-1 and because the geometric mean of two positive quantities lies below the arithmetic mean:

$$|\rho_{12}| < \sqrt{\rho_{11} \rho_{22}} < \frac{1}{2} (\rho_{11} + \rho_{22})$$

The denominator in eq. 2-6 is therefore always positive. However, it may very well be that  $\rho_{12} > \rho_{21}$ ; but then because of eq. 2-1  $\rho_{11} > \rho_{22}$ . In this case  $I_1 > I_2, I_1 < 0$ . The current in the first branch flows opposite to the input current, an impossible occurrence in normal conduction.<sup>1</sup> After they were derived theoretically by the author,<sup>2</sup> eq. 2-6 including the last inference, was confirmed quantitatively by Justi and Zickner.<sup>3</sup>

If a current  $I^0$  was already flowing at time  $t = 0$  with branch currents  $I_1^0$  and  $I_2^0$ , then these currents are superimposed on the system under consideration; in the first branch the current  $I_1^0 + I_1^*$  will now flow, in the second  $I_2^0 + I_2^*$ . If in particular  $I^0 = -I$ , then as can easily be computed,  $I_1^0 + I_1^* = -(I_2^0 + I_2^*)$ , and the leads carry no current. Therefore if we have introduced a current before cooling down to the superconducting state, and after the cooling we cut off the supply leads, then a persistent current remains in the ring consisting of the two branches. We recognize here a second method of producing persistent currents. This

<sup>1</sup> Under certain circumstances it may happen that the absolute value of  $I_1$  can be greater than  $I$ .

<sup>2</sup> See Chap. 1, footnote 23.

<sup>3</sup> E. Justi and G. Zickner, Phys. Z., 43, 258 (1941).

## 2. CURRENT DISTRIBUTION — PARALLEL SUPERCONDUCTORS 11

has also been proved experimentally by Justi and Zickner. If we now feed in still another current  $J'$ , then this is independent of the persistent current, and its branch currents  $J'_1$  and  $J'_2$  calculated from eq. 2-6 are superimposed on the persistent current.

(b) Equation 2-4 allows yet another interpretation. If we ask which distribution of the current  $I$  minimizes the magnetic energy  $1/2 \sum_i \rho_{ii} I_i^2$ ,

using the Lagrange undetermined multiplier  $\kappa$  we find the conditions

$$\left( \frac{\partial}{\partial I_i} \right) \left( \frac{1}{2} \sum_i \rho_{ii} I_i^2 - \kappa \sum_i I_i \right) = 0$$

$$\sum_i \rho_{ii} I_i = \kappa \quad (i = 1, 2, \dots, n) \quad (2-7)$$

However, from this and from

$$\sum_i I_i = I$$

we get the same relations between the  $I_i$  and  $I$  as from eq. 2-4. The current distribution in the branched superconducting circuit adjusts itself so as to minimize the magnetic energy.<sup>4</sup> This minimum is, according to eq. 2-6

$$\frac{1}{2} \rho_{11} I_1^2 + \rho_{22} I_2^2 - \rho_{12} I_1 I_2$$

This is important for the understanding of Sato's experiments.<sup>4</sup> In fact, in his experiment,  $\rho_{12} = \rho_{21}$  is very nearly zero. On supplying a current, no magnetic field is produced — to this approximation, the field strength remains zero at every point in space. If before feeding in  $I$  there are already two currents  $I_1^0$  and  $I_2^0$  flowing in the branches which produce a magnetic field because they are not in the ratio  $I_1 : I_2$ , then this addition of  $I$  does not change anything in the magnetic field.<sup>5</sup> A new field is merely superimposed on the old one, which in our case is zero. This conclusion also remains valid if we choose  $I^0 = -(I_1^0 + I_2^0)$ , i. e., if we simply cut off the leads. All this had been found experimentally by Sato in 1926 and it was his work that instigated the discussion presented here.

According to eq. 2-5

$$(\rho_{11} - \rho_{21}) I_1 - (\rho_{22} - \rho_{12}) I_2 = 0$$

In the approximation used here, which allows us to ascribe its own induction coefficient to each of the two unclosed branches (strictly speaking only for closed circuits), the left-hand side of this equation is the flux of induction through the superconducting ring formed by the two branches. The fact that the flux of induction retains its initial value, i. e., zero, even if currents are switched on, corresponds to a theorem which will be discussed in general in Chap. 12.

<sup>4</sup> G. J. Sato, Thesis, Leiden, 1926.

(e) The experiments under discussion not only confirm the complete disappearance of the resistances  $r_s$  but also show that there is no noticeable magnetic energy. Such an energy would have to be added to the energy in the principle of least action, equation 2-2, and would disturb the linearity of the relations between the  $J_s$  and  $I_s$ , if it were a quadratic function of the  $J_s$ . Otherwise it would at least cause the induction coefficients applicable to these experiments to deviate from the  $\mu_0$  values as measured with ohmic currents. Neither possibility occurs in practice. We shall find appear, but that in the experiments under discussion and in many similar experiments, it is far too small an amount to show up against the magnetic energy.

As we indicated in Chap. 1 (c), superconductors have an ohmic resistance for varying currents, in spite of the fact that their d. c. resistance is zero.

In the measurements mentioned in this paragraph however the variations were much too slow for this effect to be appreciable.

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$$\mathbf{H} = \mu \mathbf{H} + \mathbf{M} \quad (3-2)$$

Here  $\mu$  is a constant depending only on temperature, taken to be unity for ferromagnetics where  $M$  is not zero. Hysteresis effects are not included in eq. 3-2, it is true, except implicitly in the behavior of  $M$ . In Lorentz units, which we shall use throughout unless specifically stated otherwise, the Maxwell equations themselves now have the form

$$\begin{aligned} I. \quad & \text{curl } \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} & II. \quad & \text{curl } \mathbf{H} = \frac{1}{c} \left( \frac{\partial \mathbf{B}}{\partial t} + \mathbf{j} \right) \\ III. \quad & \text{div } \mathbf{H} = 0 & IV. \quad & \text{div } \mathbf{D} = \rho \end{aligned}$$

$\rho$  is the space charge density.

(b) For the superconductor we put  $\epsilon = 1$  from the outset, as Maxwell's theory does for all metallic conductors. An important feature of London's generalization is that the permeability  $\mu = 1$ . Moreover,  $M = 0$ , because no ferromagnetic material shows superconductivity. So D coincides with B and with H. Equations I — IV are simplified to

$$\begin{aligned} I. \quad & \text{curl } \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} & II. \quad & \text{curl } \mathbf{H} = \frac{1}{c} \left( \frac{\partial \mathbf{B}}{\partial t} + \mathbf{j} \right) \\ III. \quad & \text{div } \mathbf{H} = 0 & IV. \quad & \text{div } \mathbf{E} = \rho \end{aligned}$$

Now — and this introduces something essentially new — the current  $I$  and the density  $\rho$  are each split into two parts by this theory, namely the ohmic current  $i^0$  together with the appropriate density  $\rho^0$ , and the supercurrent  $i^s$  with the corresponding density  $\rho^s$ .

V

$$I = i^0 + i^s \quad \rho = \rho^0 + \rho^s$$

Between each sort of current and the corresponding density we assume a continuity equation:

$$VI \quad \text{div } i^0 + \frac{\partial \rho^0}{\partial t} = 0, \quad \text{div } i^s + \frac{\partial \rho^s}{\partial t} = 0$$

$$\mathbf{D} = \epsilon \mathbf{E} \quad I = \sigma \mathbf{E} \quad (3-1)$$

The dielectric constant  $\epsilon$  and the conductivity  $\sigma$  are positive constants of the material depending only on temperature. For the magnetic field we need three more vectors  $H$ ,  $B$ , and  $M$ , i. e., the field intensity, the magnetic induction, and the induction due to permanent magnetization present only in permanent magnets that may be in the field. For these we have the relation

Equation VI gives a definite meaning to the coupling of  $\rho^0$  with  $i^0$  and of  $\rho^s$  with  $i^s$ . Only the continuity equation for the total current  $I$  and the total density  $\rho$  follows in the known way from I, II, and IV'. The subdivision carried out here therefore represents an essentially new assumption. Incidentally,  $\rho^0$  shall include not only the contribution from the mobile carriers of the ohmic current  $i^0$  but also that from the fixed atoms which is constant in time, and for a homogeneous superconductor uniform in space. This is completely consistent with eq. V'1.  $\rho^s$  shall be due only to the carriers of the supercurrent. We are forced to this assertion because in eq. 13-10  $\rho^s$  appears as a factor in a product which can be related only to the supercurrent.

<sup>1</sup>P. London, Une conception nouvelle de la supraconductivité. *Paris*, 1937.

<sup>2</sup>N. V. Lur'e, (a) *Z. Physik*, 48, 69 (1949); (b) 48, 223 (1949); (c) 8, 185 (1948);

(d) 8, 31 (1949); (e) 8, 40 (1949); (f) Z. *Physik*, 126, 517 (1949).

For the ohmic current, Ohm's law, i. e., a linear relationship between  $\mathbf{P}$  and  $\mathbf{E}$ , shall still be valid in superconductors. For a crystal, it always has the form

$$\mathbf{I}^0 = \sum_j \sigma_{\alpha\beta} \mathbf{E}_j$$

and for mathematical reasons  $\sigma_{\alpha\beta}$  is a tensor of the second rank which we call the conductivity tensor. For cubic crystals it simplifies to a scalar conductivity  $\sigma$ , and eq. VII is replaced by the equation

$$\mathbf{I}^0 = \sigma \mathbf{E}$$

The  $\sigma_{\alpha\beta}$  are of the dimensions  $\text{A}^{-1}$ . The order of magnitude of  $\sigma$  and likewise the principal values  $\sigma_{\alpha\beta}$  of the tensor for normally conducting pure metals at the low temperatures under discussion is of the order  $10^{13} \text{ sec}^{-1}$ . According to experiments to be described in Chap. 16, we may also ascribe the same order of magnitude to the superconductor in spite of the fact that actual measurements are not available.

Finally, London's fundamental equations for the supercurrent appear as essentially new equations in the theory. We formulate them for an arbitrary crystal by associating with the vector  $\mathbf{G}$  a vector  $\mathbf{G}$  for the supercurrent per unit charge and by postulating a linear relation between them in terms of the tensor  $\lambda_{\alpha\beta}$  the sums being over  $\alpha, \beta = 1, 2, 3$ :

$$\mathbf{G}_0 = \sum_j \lambda_{\alpha\beta} \mathbf{I}_j$$

which simplifies for cubic crystals to read

$$\mathbf{G} = \lambda \mathbf{I}^0$$

And for  $\mathbf{G}$  we introduce the following two differential equations due to London:

$$\text{IX } \frac{\partial \mathbf{G}}{\partial t} = \mathbf{E}$$

$$\text{X } \mathbf{c} \cdot \nabla \mathbf{G} = -\mathbf{H}$$

According to Chap. 1 (c) London's constant  $\lambda$  is a function of temperature that increases beyond all limit as we approach the transition temperature

\*This tensor was introduced by M. von Laue (see footnote 2d).

\*These equations can be combined relativistically in the form

$$c \left( \frac{\partial P_{\alpha\beta}}{\partial x_n} - \frac{\partial P_{\beta\alpha}}{\partial x_n} \right) = M_{\alpha\beta n} \quad m, n = 1, 2, 3,$$

if one puts  $M_{11} = -M_{22}$ , etc.,  $M_{13} = H_x$ , etc., and  $x_1 = t$ ; the four vector  $\mathbf{P}$  is reduced to the supermomentum by identifying  $P_{\alpha\beta} = U_{\alpha\beta}$ ,  $\alpha = 1, 2, 3$ , and  $P_4 = 0$  for the system at rest.

Here we have written  $x_1$ ,  $x_2$ , and  $x_3$  for  $x$ ,  $y$ ,  $z$ , but this can scarcely lead to any misunderstanding.

### 3. FUNDAMENTAL EQUATIONS

from below. The tensor  $\lambda_{\alpha\beta}$  must have the same property. The dimensions of its components are [time]<sup>1</sup>.

The most general tensor of second rank is asymmetric, but from Table I-1 all the crystal classes in which superconductivity has been observed have such high crystallographic symmetry that all tensor constants must be symmetrical, i. e., interchanging their suffixes does not change their value.\* We therefore put

$$\begin{aligned} \sigma_{\alpha\beta} &= \sigma_{\beta\alpha} \\ \lambda_{\alpha\beta} &= \lambda_{\beta\alpha} \end{aligned} \quad (3-5)$$

In Chap. 13 (b) this will turn out to be a necessary condition for the possibility of superconductivity. It can also be understood in this way why deformations which distort the natural symmetry of the crystals easily destroy the superconductivity — as has often been observed. We shall find in Chap. 5 that

$$\frac{1}{2} (\mathbf{I}^0 \cdot \mathbf{G}) = \frac{1}{2} \sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{I}_{\alpha} \mathbf{I}_{\beta} \quad (3-4)$$

is the density of the free energy that is connected with the supercurrent. By requiring that it positive, not only in the cubic system where it equals  $\frac{1}{2} \lambda (\mathbf{I}^0)^2$ , but also under all circumstances, we conclude that the components  $\lambda_{\alpha\beta}$  with two identical suffixes, the determinant of all the  $\lambda_{\alpha\beta}$ , and the three symmetrical subdeterminants

$$\begin{vmatrix} \lambda_{111} & \lambda_{112} & \lambda_{113} \\ \lambda_{121} & \lambda_{222} & \lambda_{223} \\ \lambda_{131} & \lambda_{231} & \lambda_{333} \end{vmatrix}$$

are all positive. These are the necessary and sufficient conditions that the quadratic form  $\sum \lambda_{\alpha\beta} I_{\alpha} I_{\beta}$  shall be positive and definite. But as  $\sigma_{\alpha\beta} \mathbf{E}_{\alpha} \mathbf{E}_{\beta}$  is also positive and definite (it is the expression for the Joule heat, see Chap. 5), the conductivity tensor obeys the same conditions. The quadratic surfaces corresponding to these tensors:

$$\sum_{\alpha\beta} \lambda_{\alpha\beta} x_{\alpha} x_{\beta} = \text{constant} \quad \text{and} \quad \sum_{\alpha\beta} \sigma_{\alpha\beta} x_{\alpha} x_{\beta} = \text{constant}$$

are therefore ellipsoids. If their axes are chosen as coordinates, then all the tensor components with unlike suffixes vanish, and those with two like suffixes give the principal values  $A_1, A_2, A_3$  of the tensor.

In the crystal classes in which superconductivity has been detected to date (Table I-1) the axes of these ellipsoids are completely fixed and

\*This is also true for all superconducting compounds and alloys. Compare Max von Laue, footnote 2d; in this reference, a table appears giving all crystal classes together with the properties of all second-rank tensors that can belong to them, like the tensors  $\lambda_{\alpha\beta}$  and  $\sigma_{\alpha\beta}$ , that can form a linear relation between two polar vectors. In these particular cases the polar vectors are  $\mathbf{u}$  and  $\mathbf{v}$ ,  $\theta$ , and  $\mathbf{E}$ .

coincide with the principal crystallographic axes. In the rhombic system, i.e., for gallium and uranium, they are mutually perpendicular but not of equal length. In the tetragonal and hexagonal systems the surfaces are crystallographic axes. Therefore two of the principal values of the tensor  $\lambda_{\alpha\beta}$  are equal. We need scarcely mention the cubic system for which the ellipsoid degenerates into a sphere.

As the determinant of  $\lambda_{\alpha\beta}$  differs from zero the three equations VIII can be solved for the components  $I_{\alpha\beta}$ . Thus not only does it follow from  $\rho = 0$  that  $G = 0$ , but also conversely from  $G = 0$  that  $I_{\alpha\beta} = 0$ . From the supercurrent feature of this theory that the ohmic current and coupled in a secondary way through the magnetic field with which they are both related.

Equation III<sub>1</sub> is given by forming the divergence of  $X$ ; eq. I<sub>1</sub> by forming the curl of eq. IX and using eq. X. Nevertheless by retaining eqs. I<sub>1</sub> and III<sub>1</sub> Maxwell theory, but only supplements it. There is no contradiction in the system of equations.

(c) In addition to the differential equations, the theory still needs to be completed by boundary conditions at all surfaces where the constants of the theory undergo sudden changes, as at the surfaces of the specimens. Such boundary conditions do not represent new additions; they are limiting forms of the differential equations themselves. For instance B, D, and I have finite time derivatives everywhere, and hence eqs. I and II lead through Stokes theorem (regarded as applying to a "surface curl") to the any surface. Also, according to eq. III<sub>1</sub> we may say that the "surface divergence" of B is zero; therefore if we indicate two opposite normals of the surface of discontinuity by  $n_1$  and  $n_2$  we obtain

$$B_{n_1} + B_{n_2} = 0 \quad (3-5)$$

Similarly, according to eq. IV, when a surface charge density exists we have

$$D_{n_1} + D_{n_2} = \rho \quad (3-6)$$

These two equations hold for the superconductor if we replace B by H and D by F. The following new boundary conditions then have to be added: according to the continuity equations in eq. VI the surface divergences of the current densities  $\rho^1$  and  $\rho^2$  related to the surface charge densities  $\rho^1$  and  $\rho^2$  by the equations:

$$I_{n_1} + I_{n_2} \approx \frac{\partial \rho^0}{\partial t} \quad I_{n_1} + I_{n_2} \approx \frac{\partial \rho^1}{\partial t} \quad (3-7)$$

Finally because H is finite everywhere, eq. X requires that the tangential components of (i) the everywhere continuous across every surface:

### 3. FUNDAMENTAL EQUATIONS

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(3-8)

$G_{ii} = G_{ij}$ ,  
This means that at the boundary between two cubic crystal superconductors

(3-9)

$\lambda_{ij} I_{ij} = \lambda_{ij} I_{ij}$ .  
The superconductor with the smaller  $\lambda$  carries the higher tangential current; it behaves as if it were the better superconductor. Increasing temperature increases the constant, as already stated, thus impairing the superconductor.

(d) Although, as already mentioned, we shall generally use Lorentz units, we have also enumerated the changes involved in the transition to electrostatic units. In these units the fundamental eqs. II and IV become

$$\text{curl } H = \frac{1}{c} \left( \frac{\partial D}{\partial t} + 4\pi\rho \right) \quad \text{and} \quad \text{div } D = 4\pi\rho \quad (3-10)$$

Equations I, III, and VII remain unchanged. In general, the transformation is effected by the equations:

$$\rho_L = \sqrt{4\pi\rho_{av}}, \quad I_{L\alpha} = \sqrt{\frac{4\pi}{\lambda}} I_{\alpha}, \quad K_{L\alpha} = \frac{E_{av}}{\sqrt{4\pi}}, \quad (3-11)$$

$$H_{L\alpha} = \frac{G_{av}}{\sqrt{4\pi}}, \quad B_{L\alpha} = \frac{B_{av}}{\sqrt{4\pi}}, \quad (\sigma_{av})_{L\alpha} = 4\pi(\sigma_{av})_{av} \quad (3-10)$$

The question arises: shall the tensor components  $\lambda_{\alpha\beta}$  have the same values in both systems so that  $G_{L\alpha} = \sqrt{\frac{4\pi}{\lambda}} G_{\alpha}$  and the eqs. IX and X have to be replaced by

$$4\pi \frac{\partial G_{av}}{\partial t} = E \quad \text{and} \quad 4\pi \text{curl } G_{av} = -H? \quad (3-12)$$

We decide instead in favor of taking over eqs. IX and X unchanged in the electrostatic system and derive the transformations:

$$G_{L\alpha} = \frac{G_{av}}{\sqrt{4\pi}}, \quad (\lambda_{ab})_{L\alpha} = \frac{(\lambda_{ab})_{av}}{4\pi}. \quad (3-11)$$

We shall find out the advantages of this convention in Chaps. 15 and 16. There the pure number  $\sigma \cdot \lambda$ , where  $\sigma$  is a frequency, has the same value in both systems of units, and plays an important part by the scalar product  $(\nu \cdot \theta)$  in what follows.

(e) Even though we intend to present London's theory in a phenomenological manner, we wish nevertheless to point out the atomic theory basis from which it developed historically. Fritz and Heinz London attempted in 1935 to make the fundamental eqs. IX and X, which they wrote in the form

$$1X_{at} \quad \frac{\partial I_{av}}{\partial t} = E \quad N_{av} \quad \text{curl } (\vec{I}, \vec{P}) = -H \quad (3-12)$$

\*F. and H. London, *Physica*, 2, 241 (1935).

seem plausible from quantum theoretical considerations. In this way they found a relation between the constant  $\lambda$  and the charge  $e$ , the mass  $m$  of the electron, and the number  $N$  of the superconducting electrons per unit volume, namely,

$$\lambda = \frac{m}{e^2 N} \quad (3-12)$$

However, eq. IXA had already been derived in 1933 by Becker, Heller, and Sauter,<sup>7</sup> on a purely mechanical basis. They took the electric field as the only force acting on the electron, so that

$$m \frac{de}{dt} = e E$$

where  $e$  is the velocity of the electron. Furthermore, as the current density is  $i = e N v$  one arrives at eqs. IXA and 3-12 if one neglects the difference between the partial time derivative  $d/dt$  (at constant coordinates) and  $d/dt$  referring to a moving particle: this is permissible for sufficiently small velocities. Equation IXA can be derived from eq. IXA by means of Maxwell's equation I under the physically self-evident assumption that no field existed prior to a certain time 0. Thus if one takes the curl of eq. IXA and integrates from  $t = 0$  to  $t$ , one gets:

$$\text{curl} (1/t) = \int \text{curl} E dt \xrightarrow{t=0} -\frac{1}{c} H$$

To this extent this entire theory was contained in the "acceleration theory" of Becker and co-workers.

We shall not go further into this atomic picture here although in Chap. 13 we shall make use of the picture to explain the Maxwell-London stresses, assuming that neither the lattice formed by the ions nor the ohmic conduction electrons exert any force on the mechanism of the supercurrent.

To make a rough estimate of  $\lambda$  from 3-12 we take aluminum as an example. The lattice cell contains four atoms and has an edge of  $4 \times 10^{-8}$  cm. In one cubic centimeter therefore there are  $1.6 \times 10^{22}$  cells and  $6.4 \times 10^{22}$  same, with  $m = 9 \times 10^{-31}$  gm and  $e = (4 \pi \epsilon_0) / (4 \pi \times 4.8 \times 10^{-10} = 1.7 \times 10^{-19}$  Lorentz unit, it follows that

$$\lambda_{Al} = 2 \times 10^{-21} \text{ sec}^2 \quad (3-13)$$

or according to 3-11,

$$\lambda_{Al} = 2.5 \times 10^{-21} \text{ sec}^2$$

But probably the number  $N$  is much smaller, and  $\lambda$  accordingly greater.

#### CHAPTER 4

##### Space Charges in Superconductors

Space charges may be formed in a superconductor by irradiating it with fast cathode rays which are sooner or later trapped inside the superconductor. This theory must lead to plausible conclusions about the future of such charges, and this requirement has played a role in its development. We assume the crystal to be cubic,  $\lambda$  and  $\rho$  constants in space and time. From eqs. VI, IXA, and IVa respectively there follow the equations

$$\frac{\partial \rho^0}{\partial t} = -\text{div} \mathbf{B} = -\frac{1}{\lambda} \text{div} \mathbf{R} = -\frac{\rho^0 + \rho^1}{\lambda} = -\frac{(\rho^0 + \rho^1)}{\lambda},$$

while from eqs. IVa, VIIa, and VIIa correspondingly

$$\rho^0 = \text{div} \mathbf{E} = \frac{1}{\sigma} \text{div} \mathbf{j}^0 = -\frac{1}{\sigma} \phi^0$$

Therefore the differential equations

$$\frac{\partial \rho^0}{\partial t} + \frac{(\rho^0 + \rho^1)}{\lambda} = 0 \quad (4-1)$$

hold for the two unknowns  $\rho^0$  and  $\rho^1$ . They are solved under the assumption that  $\rho^0 = P^0 e^{-\alpha t}$ ,  $\rho^1 = P^1 e^{-\alpha t}$ , which transform the differential equations into the algebraic relations

$$(a^2 + \lambda^{-1}) P^1 + P^0 + \lambda^{-1} P^0 = 0 \quad (4-2)$$

$$\sigma P^0 + (\sigma - \alpha) P^0 = 0 \quad (4-3)$$

$$\sigma^2 - \sigma \alpha + \lambda^{-1} \alpha = 0 \quad (4-4)$$

$$P^0/P^1 = -\frac{1}{\lambda} \left( 1 - \frac{1}{\sigma^2/\lambda} \right) \quad (4-5)$$

$$P^1/P^0 = -\frac{1}{\lambda} \left( 1 + \sqrt{1 - \frac{4}{\sigma^2/\lambda}} \right) \quad (4-6)$$

$$P^0/P^2 = -\frac{1}{\lambda} \left( 1 - \sqrt{1 - \frac{4}{\sigma^2/\lambda}} \right) \quad (4-7)$$

$$P^2/P^0 = -\frac{1}{\lambda} \left( 1 + \sqrt{1 - \frac{4}{\sigma^2/\lambda}} \right) \quad (4-8)$$

$$a_3 = 0,$$

$$a_2 = 0,$$

$$a_1 = 0,$$

$$a_0 = 0,$$

$$P^0 = A_1 e^{-\alpha t} + A_2 e^{-\alpha t} + A_3$$

$$\rho^0 = -\frac{1}{2} \left( 1 - \sqrt{1 - \frac{4}{\sigma^2/\lambda}} \right) A_1 e^{-\alpha t} - \frac{1}{2} \left( 1 + \sqrt{1 - \frac{4}{\sigma^2/\lambda}} \right) A_2 e^{-\alpha t} - A_3$$

<sup>7</sup> R. Becker, U. Heller, and F. Sauter, Z. Physik, **85**, 772 (1935).

$A_1, A_2, A_3$  are constants of integration, i. e., invariable with time, but otherwise arbitrary functions of position.  $\sigma_1$  and  $\sigma_2$  can be complex, but both roots always have real parts. When  $\sigma_1$  and  $\sigma_2$  are complex, but superposed vibrations of  $\rho^0$  and  $\rho'$  which decay with time until  $\rho = \rho^0 + \rho'$  becomes zero. The equations do not require that the individual densities  $\rho$  and  $\rho'$  each vanish. This is related to the fact that the two mechanisms of conduction are independent, being coupled only by the field which has already disappeared in the final state when the total density  $\rho = 0$ .

On the whole the phenomenological theory does not say anything about the individual densities in the final state, except that where a current  $I$  is flowing,  $\sigma^2$  cannot be zero. Otherwise it is assumed that where a current  $I$  is current, which we shall meet with in eq. 13-10, the momentum  $p^2/2\rho$  of the supercurrent is equal to the momentum  $p^2/2\rho'$  of the supercurrent having a density  $\rho'$  and is superimposed upon, all other processes taking place in the superconductor. When we investigate these other processes, therefore, we neglect the space charge completely and always put  $\operatorname{div} E = 0$  in place of IV'.

In order to do this it is necessary that  $\sigma$  and  $\lambda$  do not change in time or example, or varying composition of an alloy, then the space charges would change according to other laws. Nevertheless in a stationary state the superconductor is charge free under all circumstances. From eq. VIII it follows, namely, that if  $\partial/\partial t = 0$ , then  $E = 0$ , and therefore according to IV,  $\rho = 0$ . The above calculation cannot be applied to a noncubic crystal, where  $\sigma$  is a symmetrical tensor. However, in the next chapter we will show how we can also draw conclusions about the decay in this case. In a normal conductor with a cubic lattice the charge decays according to  $c^{-t/\tau}$  as can be seen by forming the divergence of eq. III. This result is well known, but having regard to the magnitude of  $\sigma$  it is doubtful whether the Maxwell theory will still be valid for such a rapid decay. However, it is also doubtful in our theory of superconductivity. However, it is significant that the theory does lead to plausible results, and its conclusions about the decay should be at least qualitatively correct.

The result is immediately

$$-\epsilon \operatorname{div} [E \times H] = \left( E \cdot \frac{\partial D}{\partial t} \right) + \left( H \cdot \frac{\partial B}{\partial t} \right) + (E \cdot I) \quad (5-2)$$

According to eqs. 3-1 and 3-2 and because  $\partial M/\partial t = 0$ , this takes the form

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \epsilon E^2 + \frac{1}{2} H^2 \right) + \sigma E^2 + \operatorname{div} [E \times H] = 0 \quad (5-3)$$

Within the differential sign are the density of electrical energy  $\frac{1}{2}\epsilon E^2$  and of magnetic energy  $\frac{1}{2}\mu H^2$ .  $\sigma E^2$  gives the Joule heat per unit time, and  $\epsilon [E \times H]$  is the flux density of electromagnetic energy, the so-called Poynting vector.

Proceeding in the same manner with eqs. I, and II, we find for the interior of the superconductor, instead of eq. 5-2

$$-\epsilon \operatorname{div} [E \times H] = \left( E \cdot \frac{\partial D}{\partial t} \right) + \left( H \cdot \frac{\partial B}{\partial t} \right) + (E \cdot I) + (E \cdot \eta) \quad (5-4)$$

or, also according to eqs. VII, VIII, and IX

$$\frac{\partial}{\partial t} \left( \frac{1}{2} E^2 + \frac{1}{2} H^2 + \frac{1}{2} \sum_{ab} j_a j_b \epsilon_{ab} \right) + \sum_{ab} \sigma_{ab} E_a F_b + c \operatorname{div} [E \times H] = 0 \quad (5-5)$$

In a superconductor there is, in addition to the electric and magnetic energy, a specific energy of the supercurrent having a density

$$\frac{1}{2} \sum_{ab} j_a j_b \epsilon_{ab} = \frac{1}{2} (I \cdot \eta) \quad (5-6)$$

or, for the cubic case

$$\frac{1}{2} \sum_{ab} j_a j_b = \frac{1}{2} (I \cdot \eta^2) \quad (5-7)$$

This is the only difference from the older theory. If we wish to combine the laws of conservation, eqs. 5-3 and 5-5, which will be useful later, we put

$$\frac{1}{2} E^2 + \frac{1}{2} \mu H^2 + \frac{1}{2} (I \cdot \eta) \quad (5-8)$$

for the total energy density. Our assumptions in Chap. 3 (b) about the tensors  $\lambda$  and  $\sigma$  ensure that the two sums in eq. 5-5 are always positive. Therefore it follows from eq. 5-5 that the energy of any electric field will be entirely dissipated by Joule heat if energy is not supplied from outside.

Therefore if the superconductor does contain space charges, they must vanish. For if they were assumed to remain, there would exist an electric field without a magnetic field strength: the Poynting vector would be zero, and according to eq. 5-5 the field energy would decrease until the field and therefore also its charges become zero, contradicting the hypothesis. The conclusion drawn in Chap. 4 about the decay of the total space charge density  $\rho$  in superconductors with a cubic lattice structure is in this way applicable to all superconductors.

Stationary magnetic fields are, however, possible in which a supercurrent appears but no electric field strength. In deriving the energy law,

$$(a) \text{ We obtain the energy principle for the space outside the superconductor in the known manner by forming the scalar product of eq. I with } (-H) \text{ and of II with } E, \text{ adding the results and applying the rule } (P \cdot \operatorname{curl} Q) - (Q \cdot \operatorname{curl} P) = \operatorname{div} [Q \times P] \quad (5-1)$$

## CHAPTER 5

### The Conservation of Energy

eq. 5-5, it is assumed that the  $\lambda_{\mu}$ 's do not change with time, just as in eq. 5-2  $\epsilon$  and  $\mu$  have to be constant. All these constants of the material depend on temperature. Therefore eqs. 5-2 and 5-5 can be used for isothermal processes only. The kinds of energy appearing here are therefore free energies in the sense of thermodynamics. The actual energy  $E$  is connected with the free energy  $F$  by the relation  $E = F - T \frac{\partial F}{\partial T}$ . Consequently the energy of the superconductor per unit volume is

$$\frac{1}{2} \sum_{\sigma\mu} \left( \lambda_{\sigma} - T \frac{\partial \lambda_{\mu}}{\partial T} \right) \mathbf{L}_{\sigma} \mathbf{L}_{\mu}$$

or for the cubic case

$$\frac{1}{2} \left( \lambda - T \frac{\partial \lambda}{\partial T} \right) \mathbf{L}^3$$

Reversing signs, the second terms, i. e., the expressions

$$\frac{1}{2} \mathcal{T} \sum_{\sigma\mu} \frac{\partial \lambda_{\mu}}{\partial T} \mathbf{L}_{\sigma} \mathbf{L}_{\mu} \quad \text{or} \quad \frac{1}{2} T \frac{\partial \lambda}{\partial T} \mathbf{L}^3$$

represent the heat which has to be removed from the superconductor during isothermal production of the supercurrent  $I$ . As  $\lambda$  increases with  $T$  they are positive, and immediately below the transition temperature they are quite considerable.

eq. 5-5, it is assumed that the  $\lambda_{\mu}$ 's do not change with time, just as in eq. 5-2  $\epsilon$  and  $\mu$  have to be constant. All these constants of the material depend on temperature. Therefore eqs. 5-2 and 5-5 can be used for isothermal processes only. The kinds of energy appearing here are therefore free energies in the sense of thermodynamics. The actual energy  $E$  is connected with the free energy  $F$  by the relation  $E = F - T \frac{\partial F}{\partial T}$ . Consequently the energy of the superconductor per unit volume is

$$-\Delta \mathbf{H} = \frac{1}{c} \left\{ \operatorname{curl} \left( \frac{\partial \mathbf{E}}{\partial t} + \operatorname{curl} \mathbf{E} + \operatorname{curl} \mathbf{H} \right) \right\}$$

We transform the right-hand side of this by means of eqs. I<sub>1</sub>, VII, and IX, the first term yields  $-(1/c^2) \partial \mathbf{H} / \partial t^2$ , the second  $-(\sigma/c^2) \partial \mathbf{H} / \partial t$ , and the third  $-\mathbf{H} / c^2 \mathbf{L}$ . Consequently

$$W(\mathbf{H}) \equiv \Delta \mathbf{H} - \frac{1}{c^2} \frac{\partial \mathbf{H}}{\partial t^2} - \frac{\sigma}{c^2} \frac{\partial \mathbf{H}}{\partial t} - \frac{\mathbf{H}}{c^2 \mathbf{L}} = 0 \quad (6-2)$$

Now we form the curl of eq. I<sub>1</sub>. Because of IV', with  $\rho = 0$  the only term we get on the left-hand side is  $-\partial^2 \mathbf{E} / \partial t^2$ . By using eqs. II, and VII, then eqs. VIII and IX we reduce the right-hand side to

$$\begin{aligned} -\frac{1}{c} \operatorname{curl} \frac{\partial \mathbf{H}}{\partial t} &= -\frac{1}{c^2} \left( \frac{\partial \mathbf{E}}{\partial t^2} + \frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{E}}{\mathbf{L}} \right) \\ &= -\frac{1}{c^2} \left( \frac{\partial \mathbf{E}}{\partial t^2} + \sigma \frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{E}}{\mathbf{L}} \right) \end{aligned}$$

Consequently

$$W(\mathbf{E}) \equiv \Delta \mathbf{E} - \frac{1}{c^2} \left( \frac{\partial \mathbf{E}}{\partial t^2} + \sigma \frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{E}}{\mathbf{L}} \right) = 0 \quad (6-3)$$

If we again form the curl of eq. 6-2 it follows because of eq. II<sub>n</sub>, and because the operator  $W$  can be interchanged with the operation of forming the curl:

$$W \left( \frac{\partial \mathbf{E}}{\partial t} + \mathbf{l} \right) = 0$$

By combining this with eq. 6-3 differentiated with respect to  $t$ , one gets

$$W(\mathbf{l}) = 0$$

On the other hand, multiplying eq. 6-3 by  $\sigma$  and using eq. VII give

$$W(\mathbf{l}) = 0 \quad (6-4)$$

Consequently by subtracting the last two equations, one finds from eq. V

$$W(\mathbf{l}) = 0 \quad (6-5)$$

The generalized telegrapher's equation  $W(\mathbf{u}) = 0$  therefore holds for each component of any of the field vectors with respect to cartesian coordinates. If the vectors were resolved in terms of curvilinear coordinates special treatment would be necessary.

Most experiments with superconductivity deal with stationary fields, so that their study constitutes the most important part of the theory. For

## CHAPTER 6

### The Telegrapher's Equation for Superconductors with Cubic Crystal Structure

It is known that by eliminating all field vectors but one from among the remaining vector, the so-called telegrapher's equation which occupies A position intermediate between the wave equation  $\partial^2 u / \partial t^2 - (1/c^2) \partial^2 u / \partial x^2 = 0$  and the equation for heat conduction  $\partial u / \partial t - k^2 \partial^2 u / \partial x^2 = 0$ . We now wish to perform this elimination for the superconductivity theory. We assume all constants of the material to be unvarying in time and space. The lattice shall be cubic. We form the curl of I<sub>1</sub>. Then from the rule

$$\operatorname{curl} \operatorname{curl} \mathbf{P} = \mathbf{grad} \operatorname{div} \mathbf{P} - \Delta \mathbf{P} \quad (6-1)$$

<sup>1</sup>This is the Helmholtz (free energy)  $F = E - TS$ , not the Gibbs free energy  $G = E - TS + P V + H M$ .

this case the equation for  $\mathbf{H}(\mathbf{r})$  is reduced to its first and its last terms:

$$d\mathbf{u} - \beta^2 \mathbf{u} = 0 \quad (6-6)$$

where  $\mathbf{u}$ , as stated, represents a component of any field vector and where

$$\beta^2 = \frac{1}{e^2 A} \quad (6-7)$$

Chaps. 7 and 11 will deal with this differential equation. All the above last two terms in eq. 6-1 gain a factor  $4\pi$ . So in place of eq. 6-7

$$\beta^2 = \frac{4\pi}{e^2 A} \quad (\text{in esu}) \quad (6-8)$$

According to eq. 3-11  $\beta$  has the same value in both systems of units.

## CHAPTER 7

### Stationary Fields

(a) As mentioned in Chap. 4 it follows from eq. IX that  $\mathbf{E} = 0$  in the stationary case. Furthermore by eq. 4-1,  $\mathbf{E}$  is the gradient of a scalar potential and so the superconductor is a region of constant potential  $\phi$  when the tensor components  $A_{\mu}^{\alpha}$  vary with position in space. By eq. VII presence of the supercurrent; it is dependent of its potential gradient by experiment using direct current can enable us to detect the finite conductivity of the superconductor. The only significant field vectors are the current  $\mathbf{j}$  and the magnetic field  $\mathbf{H}$ . These vectors are more strongly coupled than in the normal conductor because there exists between them not only the generally valid relation  $\mathbf{H} = \mathbf{j}/\mu_0$ , which here simplifies to

$$\text{curl } \mathbf{H} = \frac{\mathbf{j}}{\mu_0} \quad (7-1)$$

but also eq. IX applying specifically to superconductors:

$$\text{curl } \mathbf{G} = -\frac{\mathbf{H}}{\mu_0}, \quad \left( \mathbf{G}_a = \sum_b \lambda_{ab} \mathbf{l}^b \right) \quad (7-2)$$

Everything we can say about the stationary case is based on the combined application of these two laws. This excludes the possibility of a current-free magnetic-potential field in a normal conductor. From  $\text{curl } \mathbf{H} = 0$  it follows that  $\mathbf{j} = 0$ ,  $\mathbf{G} = 0$ , and  $\mathbf{H} = 0$ . Strictly speaking there is no

## 7. STATIONARY FIELDS

outside field into which one could place a superconductor carrying a current. The current distribution changes with any attempt to do so in such a way as to annul the outside field. It is possible to keep the current strength constant, and if one considers only the total current strength, one may use the term "exterior field". In the following sections we shall follow this through for the superconductor with cubic crystal structure.

In many of the examples to be considered the field inside the superconductor is desired when the field in the surrounding space is known. It follows from a general theorem that the solution is unique. In fact, if we form the scalar product of eq. 7-1 with  $\mathbf{G}$  and of eq. 7-2 with  $(-\mathbf{H})$ , add the two, and apply the rule 5-1, we obtain

$$\text{div} (\mathbf{H} \times \mathbf{G}) = \frac{1}{c} \{ (\mathbf{l} \cdot \mathbf{G}) + \mathbf{H}^2 \} \quad (7-3)$$

Integrating eq. 7-3 over the volume of the superconductor and using Gauss' theorem,<sup>1</sup>

$$\int \text{div} (\mathbf{H} \times \mathbf{G}) \, d\tau = - \int_S [\mathbf{H} \times \mathbf{G}]_n \, da$$

we get

$$\frac{1}{c} \int_S [(\mathbf{l} \cdot \mathbf{G}) + \mathbf{H}^2] \, d\tau = \int_S (\mathbf{G} \times \mathbf{H})_n \, da \quad (7-4)$$

The suffix  $S$  below the integral signs indicates that the volume integral extends over the volume of the superconductor and the surface integral over its entire surface.<sup>2</sup>

Now the normal component of the vector product  $(\mathbf{G} \times \mathbf{H})$  contains only the tangential components of  $\mathbf{G}$  and  $\mathbf{H}$ . If either  $\mathbf{G}_t = 0$  or  $\mathbf{H}_t = 0$  over the whole surface, then the right side of eq. 7-4 is zero. The left side, however, vanishes only if  $\mathbf{H} = 0$  and  $\mathbf{G} = 0$  at every point of the superconductor.

Consider two fields  $\mathbf{H}^{(1)}$  and  $\mathbf{H}^{(2)}$  which coincide everywhere over the boundary either with respect to  $\mathbf{H}_{\text{ext}}$  or to  $\mathbf{G}_{\text{ext}}$ . Equation 7-4

<sup>1</sup> $n_H$  indicates the inner normal on the surface  $da$ .

<sup>2</sup>If one uses the Gauss theorem for multiply connected regions, as we do later in Chap. 12, it is first necessary to produce singly connected regions by making a sufficient number of cuts and adding the new cross sections to the surface. Sometimes the cross sections make appreciable contributions. Here this is not the case because  $\mathbf{G}$  and  $\mathbf{H}$  are singlevalued functions of position, so that the contributions from both sides of any cross section cancel each other. Equation 7-4 therefore holds also for multiply connected superconductors.

<sup>3</sup>According to eq. 3-4,  $(\mathbf{l} \cdot \mathbf{G})$  is necessarily positive with the exception of the case where  $\mathbf{l} = 0$ ,  $\mathbf{G} = 0$ .

holds equally well for the difference field  $H' = H(0) - H^0$ ,  $I' = I(0) - I^0$  because all our differential equations are linear; it follows then that the difference field vanishes throughout the volume:  $H' = 0$ ,  $I' = 0$ . The stationary field in a superconductor is therefore uniquely determined by the tangential components at its surface of either the magnetic field or of the electromagnetic momentum of the supercurrents. This corresponds with the theorem of potential theory according to which the potential gradient in a region is uniquely fixed by its tangential components over the surface; these fix the surface potential to within an additive constant, and this in turn fixes the potential in the interior. The vectors  $\mathbf{Q}$  and  $\mathbf{H}$  on the right-hand side of eq. 7-4 here refer to the inner side of the surface. It is also possible here to insert for  $\mathbf{H}$  its value on the outside of the surface because by Chap. 3 (d) the tangential component of  $\mathbf{H}$  is continuous across the surface. In this way the field in the interior is uniquely determined by the external magnetic field.

(b) For the homogeneous superconductor with a cubic lattice, eq. 7-2 can be simplified to read

$$\lambda \operatorname{curl} \mathbf{I}' = -\frac{1}{c} \mathbf{H} \quad (7-5)$$

If we form the curl of eq. 7-1, then the fundamental eq. III, and eq. 7-5 together with the theorem  $\int_{\Gamma} \mathbf{f} \cdot d\mathbf{l} = 0$  give us

$$\partial \mathbf{H} - \mu^2 \mathbf{H} = 0, \quad \rho^2 \approx \frac{1}{c^2 \lambda} \quad (7-6)$$

Conversely, if we form the curl of eq. 7-5, then use eqs. VI and 7-1, we get

$$\partial \mathbf{I}' - \mu^2 \mathbf{I}' = 0 \quad (7-7)$$

Thus we come back at once to eqs. 6-6 and 6-7.

(c) The simplest conceivable example is that of a superconductor filling one half of space  $x > 0$ , so that the plane  $x = 0$  is its boundary. If in outside space  $x < 0$ , there is a homogeneous magnetic field  $\mathbf{H}^0$ , then eq. 6-6 can be solved by putting

$$\mathbf{H} = \mathbf{H}^0 e^{-\beta z}, \quad (7-8)$$

Because  $\operatorname{div} \mathbf{H} = 0$ ,  $\mathbf{H}^0$  must be zero. We can turn the  $x$  and the (par-  
-ticular)  $y$  directions in such a manner that  $\mathbf{H}^0$  also vanishes. Then it follows that for the field strength in the superconductor

$$\mathbf{H}_x = \mathbf{H}_y = 0, \quad \mathbf{H}_z = \mu^2 e^{-\beta z}. \quad (7-9)$$

Therefore according to eq. 7-1 the equations<sup>4</sup>

$$I_x = -\frac{\partial H_z}{\partial z}, \quad \rho^2 H_x e^{-\beta z} = -\lambda^{-1} H^0 e^{-\beta z}, \quad (7-10)$$

$$I_y = I_z = 0$$

in electrostatic units  $I_x = H^0 e^{-\beta z}/(\sqrt{4\pi\lambda})$ , compare eqs. 3-10 and 3-12.

represent the supercurrent vector field. We gather from this that the current density at the surface depends only on the field strength  $H^0$  there,  $I_x, H_y$  and the inner normal of the superconductor are perpendicular to each other and form a right-handed system like the coordinate system  $x, y, z$  adopted here. The field penetrates the superconductor only to a depth of the order of magnitude  $\beta^{-1}$ . It forms a protecting layer of that thickness under which lies a region protected from the influence of the field. This result is fundamental because it can be taken over for the case of curved surfaces provided only that the superconductor is thick compared with the penetration depth  $\beta^{-1}$ . In this lies the explanation of the Meissner effect.

The surface density of the current is

$$I_x = \int_0^z dz \cdot I^0 H^0 \quad (7-11)$$

In electrostatic units eq. 7-11 reads, by eq. 3-10

$$I_x = \frac{c H^0}{4\pi} \quad (7-12)$$

and if the current is measured in amperes,  $I_x = 10 H^0/4\pi$ ; nearly 80 ampere flowing per centimeter across each magnetic line of force at  $H^0 = 100$  oersteds. The penetration depth is

$$\beta^{-1} = c/\sqrt{\lambda} \quad (7-12)$$

or  $\beta^{-1} = c/\sqrt{4\pi/4\pi}$  in electrostatic units, by eq. 7-6. It is of the order of magnitude  $10^{-4}$  cm if we assume for  $\lambda$  the order of magnitude  $10^{-1}$  sec<sup>2</sup>, which is correct according to present knowledge, for temperatures  $\frac{1}{2}\lambda$  or more below the transition temperature. Approaching the transition temperature  $T$ , it appears to increase like  $\lambda$  without limit.

(d) We now consider the field and current distribution in thin superconductors, i. e., those with thickness no longer great compared with the penetration depth. We first treat the example of a plane parallel slab extending from  $z = -d$  to  $z = +d$ . In the outside space let there be homogeneous magnetic fields  $H^-$  where  $z < -d$  and  $H^+$  where  $z > d$ , both in the  $y$  direction. The differential equation  $\partial H / \partial^2 H = 0$  and the condition  $\operatorname{div} \mathbf{H} = 0$  are satisfied by

$$H_x = H_y = 0 \quad (7-13)$$

It follows from eq. 7-1 that the current density is

$$I_x = a \cosh(\beta z) + b \sinh(\beta z) \quad (7-14)$$

<sup>4</sup> In electrostatic units  $I_x = H^0 e^{-\beta z}/(\sqrt{4\pi\lambda})$ , compare eqs. 3-10 and 3-12.

The boundary condition that  $H_y$  be continuous at  $x = \pm d$  yields two equations for the constants  $a$  and  $b$ :

$$a \cosh(\beta d) + b \sinh(\beta d) = H_y, \quad a \cosh(\beta d) - b \sinh(\beta d) = H_z \quad (7-15)$$

The solution of these is

$$a = \frac{(H_y + H_z)}{2 \cosh(\beta d)}, \quad b = \frac{(H_y - H_z)}{2 \sinh(\beta d)} \quad (7-16)$$

If  $\beta d \gg 1$ , there exists a protected region free from field and current between two protecting layers of thickness  $1/\beta$ . If  $\beta d \ll 1$ , by expanding eqs. 7-13, 7-14, and 7-16 in series we find to a first approximation

$$H_y = \frac{1}{2} (H_y + H_z) + \frac{1}{2} \frac{(H_y - H_z)x}{d}, \quad I_x = c \frac{(H_y - H_z)}{2d} \quad (7-17)$$

surface current density

$$I_x = 2d I_z = c(H_z - H_y) \quad (7-18)$$

is therefore evenly distributed over the slab, the magnetic field increases linearly with  $x$  if the field strengths differ on the two sides of the slab. If, however,  $H_y = H_z$ , no current flows, and the field is constant. If in a homogeneous magnetic field we place a sufficiently thin superconducting sheet parallel to the field strength, the field penetrates the sheet without being disturbed. For arbitrary thickness, but with  $H_y = H_z$ , eqs. 7-13 and 7-14 simplify to

$$H_y = H + \frac{\cosh(\beta x)}{\cosh(\beta d)}, \quad I_x = -H + \frac{\sinh(\beta x)}{\sqrt{k} \coth(\beta d)} \quad (7-18)^*$$

(e) Consider now the same slab with a surface current density<sup>4</sup>  $I_x$ , with certainly an even function of  $x$  as the product by  $I_x$ . The current density is equivalent, and we therefore need those solutions of the fundamental eqs. 7-14 for which  $a = -b$ . Also by eq. 7-13  $H_y$  is an odd function of  $x$ , and consequently  $H_y = -H^*$ . Thus by eq. 7-15

$$b = \frac{H_y}{\sinh(\beta d)},$$

and

$$I_x = -H^* \frac{\cosh(\beta x)}{\sqrt{k} \sinh(\beta d)}, \quad H_y = H^* + \frac{\sinh(\beta x)}{\sinh(\beta d)} \quad (7-19)$$

<sup>4</sup>With regard to the sign of  $I_x$  it must be noticed that for the boundary surface  $x = \pm d$ , the  $x$  direction is the outer normal, and not, as in eq. 7-10 the inner normal.

<sup>5</sup>Nx cannot speak of the total current in this case because the slab is unlimited in extent in the  $y$  direction.

## 7. STATIONARY FIELDS

Now we still have to calculate  $H^*$  from  $I_x$ . The equation

$$I_x = \int_{-d}^d I_s dx = -2cH^* \quad (7-20)$$

will serve for this. So the final result reads

$$I_x = \frac{1}{2} \beta I_s \frac{\cosh(\beta d)}{\sinh(\beta d)}, \quad H_y = -I_s \frac{\sinh(\beta x)}{2c \sinh(\beta d)} \quad (7-21)$$

For a thick slab ( $\beta d \gg 1$ ) one finds again that the field and current are concentrated in two protecting layers adjacent to the boundary surface. For thin sheets ( $\beta d \ll 1$ ), eq. 7-21 simplifies to

$$I_x = \frac{i_s}{2d}, \quad H_y = \frac{i_s x}{2cd} \quad (7-22)$$

The current is therefore evenly distributed through the thickness of the sheet.

(f) To generalize the results obtained from these examples a mean value theorem for scalar space functions<sup>5</sup> that obey the differential equation  $\partial u - \beta^2 u = 0$  proves to be useful. We describe a sphere of radius  $r$  around an arbitrary point  $P$  in the three-dimensional domain of the function and form the mean value over its surface satisfying the equation

$$\partial \bar{u} - \beta^2 \bar{u} = 0$$

Since however  $\bar{u}$  depends only on  $r$

$$\partial \bar{u} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \bar{u}}{\partial r} \right)$$

and the differential eq. 7-24 has the solutions

$$\bar{u} = \text{const. } \frac{\sinh(\beta r)}{\beta r} \quad \text{and} \quad \bar{w} = \text{const. } \frac{\cosh(\beta r)}{\beta r}$$

The second of these must be rejected because it increases without limit at  $r = 0$ . If we go to  $r = 0$  in the first one, we see that the constant must be  $w_P$ , therefore we find

$$w_P = \frac{\cosh(\beta r)}{\sinh(\beta r)} \quad (7-25)$$

The factor multiplying  $\bar{u}$  decreases from 1 to arbitrary small values with increasing  $r$ . For  $\beta = 0$  it would always be 1, and eq. 7-25 would go over into the well-known mean value theorem of potential theory, according to which the function  $\bar{u}$  cannot have either a maximum or a minimum at any point  $P$ . However here, with  $\beta > 0$ , the equation says only that the absolute value  $|w_P|$  is smaller than the absolute value  $|w_r|$ , excluding a maximum of  $|w_r|$  at  $P$ , but certainly permitting a minimum. The highest values of  $|w_r|$  never lie in the interior, but always on the boundary of the region in which the differential eq. 7-25 holds; for points on the surface it is not possible to construct such spheres so that eq. 7-25 does not apply.

The components  $H_x$ ,  $H_y$ , and  $H_z$  of the magnetic field strength satisfy the differential eq. 7-25; therefore we find according to this theorem that

$$(H_x)^* \leq \langle H_x^2 \rangle^{1/2}$$

However, the mean square fluctuation over the surface of the sphere,

$$\frac{1}{4\pi r^2} \int (H_x - \bar{H}_x)^2 |d\sigma| = \frac{1}{4\pi r^2} \int H_x^2 |d\sigma| - \langle H_x^2 \rangle = \bar{H}_x^2 - \langle \bar{H}_x^2 \rangle$$

is necessarily positive; therefore  $\bar{H}_x$  is positive.

$$\langle H_x^2 \rangle_p < \bar{H}_x^2$$

Since corresponding relations hold for  $H_y$  and  $H_z$ , we find by summation

$$\langle H^2 \rangle_p < \bar{H}^2$$

One can prove in the same manner that

$$\langle H^2 \rangle_p < \langle \bar{H}^2 \rangle$$

There exists no maximum of the magnetic field strength or the current density in the interior of a superconductor. The highest values of  $H^*$  and  $i^*$  are always located at the surface. The possibility of minima is demonstrated by the examples in sections (d) and (e) and also by those in the following paragraphs. This is the general theory of the Meissner effect.

If  $u$  depends only on two coordinates, the mean value is formed over a circle with radius  $r$  around the point  $P$ . Then

$$\Delta \bar{u} = \frac{1}{r} \frac{d}{dr} \left( r \frac{du}{dr} \right)$$

and eq. 7-25 is replaced by

$$\frac{\mu_0}{r} = T_0(\beta r)$$

where  $T_0(x)$  is the Bessel function of zero order to be discussed in more detail in Chap. 8. Since with increasing  $r$ ,  $T_0(\beta r)$  increases continuously from 1 and finally exceeds all limits<sup>8</sup>, all conclusions drawn from eq. 7-25 can be taken over in the two-dimensional case.

(g) However, there are limits to be set to the Meissner effect which can be derived from eq. 7-25 or 7-26. If the region where the differential  $\Delta u \ll 1$  and  $u' \approx u$ , i.e., in such a region any solution of eq. 7-25 coincides with a solution of the potential equation  $\Delta u = 0$ . Then the Meissner effect becomes undetectable. Examples are contained in the approximations 7-17 and 7-22 for the thin sheet; as a matter of fact in this case  $\bar{H}_x$  and  $H_z$  do satisfy the potential equation.

In an infinitely long straight cylinder of arbitrary but small cross section with its axis along the  $x$  direction, we can consider

$$u'_x = \text{constant}$$

<sup>8</sup>Compare the series expansion of eq. 8-6.

as the first approximation, because in this way  $\Delta u'_x = 0$ . The supercurrent is then distributed in exactly the same way as an ohmic current. If, keeping the current density  $i$ , constant, we decrease all the dimensions of the cross section by a factor  $a$ , then the magnetic field strength decreases at corresponding points like  $a$  because by Stokes' theorem it follows from eq. 11, for any surface lying entirely inside the conductor that

$$\int \mathbf{H} \cdot d\mathbf{s} = \frac{1}{c} \int i \cdot da$$

and the surface of integration decreases like  $a^3$  while the circumference decreases like  $a$ . Equation IX shows that the ratio of  $\text{curl } i$  to  $i$  decreases like  $a$ . This justifies neglecting  $\text{curl } i$  in eq. 7-25. We can take this result without hesitation for a curved wire provided that the radius of curvature is great compared with the dimensions of the cross section.

On the other hand if we place a sufficiently small superconductor of arbitrary shape in a static magnetic field of strength  $H^0$ , then the field continues unchanged through the superconductor because it obeys the differential equation  $\Delta H = 0$ . As here  $H$  is curl free, no current is produced on this approximation. This is not a contradiction of eq. 7-5 because if we integrate that equation over a surface lying entirely inside the superconductor and transform the integral on the left side to a line integral over the circumference by means of Stokes' theorem, we get

$$\int i \cdot da = - \int \mathbf{H} \cdot d\mathbf{s} \quad (7-28)$$

We apply this to two geometrically similar superconductors which may differ in their superconducting constants  $\lambda_1$  and  $\lambda_4$ . Let  $L_1$  and  $L_4$  be corresponding linear intervals. We choose two corresponding surfaces in the superconductors, the integrals on the right-hand side of eq. 7-28 are then in the ratio  $(L_1/L_4)^2$ . Corresponding parts of the circumferences however are in the ratio  $L_1/L_4$ . Consequently the ratio of the current density components  $\lambda$  at corresponding points of the two bodies is

$$\frac{\lambda_1}{\lambda_4} = \frac{\lambda_4 L_1}{\lambda_1 L_4} = \sqrt{\frac{\lambda_4}{\lambda_1} \frac{L_1}{L_4}} \quad (7-29)$$

Therefore for every sufficiently small superconductor every component  $\lambda_i$  of  $i$ ,  $i = 1, 2, 3$ , can be developed in a series the first term of which has the form

$$i_i = H^0 \tau_s \frac{\beta_i L_i}{\sqrt{L_i}} \quad (7-29)$$

The quantities  $\tau_s$  here are pure numbers, depending only on the relative positions and the shapes, but no longer on  $\lambda$  or the size of the specimen. Examples will be found in eqs. 10-2 and 11-12 as well as in the discussion following eq. 10-16.

These results do not hold without restriction for multiply connected superconductors because in this case there exist surfaces (see Chap. 12)

that extend partly outside the superconductor, in spite of the fact that their perimeters lie completely inside it. It is not then permissible to apply eq. 7-2, which is valid only for surfaces entirely within the superconductor. We shall see that in this case a persistent current, independent of  $H_0$ , can be superposed on the currents obeying eq. 7-29.

(b) According to Chap. 3 the constant  $\lambda$  is a function of temperature. Immediately below the transition temperature it is very great, and so is the penetration depth  $\beta^{-1} = c/\lambda$ . (See eq. 7-6.) Every specimen is then "small" in the sense of the present considerations; the magnetic field penetrates it undisturbed. With decreasing temperature  $\lambda$  decreases, at first very rapidly indeed. This initiates the expansion of the field — the Meissner effect. If the specimen is wrapped with a normally conducting induction coil, one can follow this process by means of the induced current; it decreases the flux of induction through the coil. Such experiments have often been carried out. In one instance Stark, Steiner, and Schonebeck observed a "paramagnetic" effect in the induced current, i. e., an effect that corresponds to an increase in flux of induction, which preceded the expansion of the field. There is as yet no explanation for this. It would not help to ascribe it to the superconductor, a permeability  $\mu$  deviating from 1. According to eq. 7-7 the former value  $1/c^2 \lambda$ , or  $\beta^4$  merely acquires a factor  $\mu$ . As the observations concern  $\beta$ , this would change the conversion from  $\beta$  to  $\lambda$ , but would offer no explanation of the deviation experiments.<sup>10</sup>

(i) We shall try to apply some of the above results to superconductors with noncubic crystal structure and consider again the simplest case: the static homogeneous magnetic field  $H_0$  in the direction of which we again take as the  $x_3$  axis. The boundary conditions for  $x_3 = 0$  are therefore

$$\begin{aligned} H_1 &= 0, & H_2 &= H^0 \quad (7-50) \\ \text{The other boundary condition is again the gradual vanishing of all field} \\ \text{vectors as } x_3 \text{ increases toward infinity. The Maxwell eq. II, } [\text{curl } H = V/c] \end{aligned}$$

<sup>10</sup>J. Stark, K. Steiner, and H. Schonebeck, *Phys. Z.*, **8**, 887 (1937).

in that the total induced current amplitude seemed to be less, occasionally even much less, than would be consistent with the complete expulsion of the field. The objection to these measurements is that the whole specimen had actually not become superconducting, so once such a ring is formed, it holds the enclosed flux of induction constant outside, as described in detail in Chap. 12, no matter how the external field is changed. The other parts remain in the intermediate state due to the influence of the field. In the superconducting ring a persistent current is produced by switching off the field, (Chap. 12). A test for this would consist in looking for the magnetic fields of such a persistent current after the external field has been switched off, but it seems that this test has never been made in such experiments.

and the London eq. X,  $(\text{curl } G_{xx} - H) = 0$  — reduce according to eq. VIII to the following:

$$\begin{aligned} I_1' &= -c \frac{\partial H_2}{\partial x_3}, & I_2' &= c \frac{\partial H_1}{\partial x_3}, \\ H_1 &= c \frac{\partial I_1'}{\partial x_3} + I_2, & H_2 &= c \left( \frac{\partial I_2'}{\partial x_3} + I_1 \right) \quad (7-31) \end{aligned}$$

$$H_3 = -c \frac{\partial I_1}{\partial x_3} - I_2, \quad \frac{\partial H_1}{\partial x_3} = -c \left( \frac{\partial I_1}{\partial x_3} + I_2 \right) \quad (7-32)$$

Because of the divergence conditions  $I_3'$  and  $H_3$  vanish. Elimination of  $I_1$  leads to the differential equations

$$\begin{aligned} \frac{\partial^2 H_1}{\partial x_3^2} - A_1 \frac{\partial H_1}{\partial x_3} - H_1 &= 0 \\ -2A_1 \frac{\partial H_1}{\partial x_3} + A_{11} \frac{\partial^2 H_1}{\partial x_3^2} - \frac{I_2'}{c^2} &= 0 \quad (7-33) \end{aligned}$$

which here replaces eq. 7-6. The most obvious way to solve this is by introducing a new coordinate system  $x_1'$  and  $x_2'$  rotated about the  $x_3$  axis, in which the tensor component  $I_{12}'$  vanishes. These are the "relative" principal axes of the tensor (i. e., relative to the plane  $x_3 = 0$ ). The most obvious principal axes of the ellipse formed by the intersection of this plane and the ellipsoid of the tensor:  $\sum \lambda_i x_i x_i = 1$  constant. This ellipse gives the "relative principal values"  $A_1'$  and  $A_2'$  of the tensor. Introducing these changes in eq. 7-33 yields at once the two solutions:

(1)  $H_1' = H_1^{(0)} e^{-A_1' x_3'/c^2} / \sqrt{A_1'}$ ,  $H_2' = 0$ ;  $(A_2' := 1/c^2 / \sqrt{A_1'})$

$I_1' = 0$ ,  $I_2' = -\sqrt{A_1'} H_1^{(0)} e^{-A_1' x_3'/c^2} / \sqrt{A_2'}$ ,  $G_3' = 0$ ,  $G_1' = 0$ ,  $G_2' = -\sqrt{A_1'} H_1^{(0)} e^{-A_1' x_3'/c^2} / \sqrt{A_2'}$ ,  $V = 0$ .

(2)  $H_1' = 0$ ,  $H_2' = H_2^{(0)} e^{-A_2' x_3'/c^2} / \sqrt{A_2'}$ ,  $I_1' = 0$

$G_1' = \sqrt{A_2'} H_2^{(0)} e^{-A_2' x_3'/c^2} / \sqrt{A_1'}$ ,  $G_2' = 0$ ,  $G_3' = 0$ .

The integration constants  $H_1^{(0)}$  and  $H_2^{(0)}$  are the external magnetic field strength components in the directions  $x_1'$  and  $x_2'$ , respectively. However, the boundary condition 7-30 must hold with  $x_1'$  and  $x_2'$  respectively. Denoting the angle between  $x_1$  and  $x_1'$  by  $\varphi$ , as in Fig. 7-1, we have to put  $H_2^{(0)} = H_2^0 \cos \varphi$ ,  $H_1^{(0)} = -H_2^0 \sin \varphi$ . Finally transforming the vector components of eqs. 7-34 and 7-35 back into the components with respect to  $x_1$  and  $x_2$ ,

$$H_1 = H_1' \cos \varphi + H_2' \sin \varphi, \quad H_2 = -H_1' \sin \varphi + H_2' \cos \varphi, \quad \text{etc.}$$

and we find

Fig. 7-1. Illustrating the transformation of coordinates to principal axes.

$$\begin{aligned}
 H_1 &= H^0 (\epsilon^{A'_1 A'_2} - \epsilon^{A'_2 A'_1}) \cos \varphi \sin \varphi \\
 H_2 &= H^0 (\epsilon^{A'_1 A'_2} - \epsilon^{A'_2 A'_1}) \cos \varphi \sin \varphi \\
 I'_1 &= H^0 \left( \frac{1}{\sqrt{A'_1}} \epsilon^{A'_1 A'_2} \cos^2 \varphi + \frac{1}{\sqrt{A'_2}} \epsilon^{A'_2 A'_1} \cos^2 \varphi + \frac{1}{\sqrt{A'_1 A'_2}} \right) \epsilon^{A'_1 A'_2} \epsilon^{A'_2 A'_1} \\
 I'_2 &= -H^0 \left( \frac{1}{\sqrt{A'_1}} \epsilon^{A'_1 A'_2} \cos^2 \varphi - \frac{1}{\sqrt{A'_2}} \epsilon^{A'_2 A'_1} \cos^2 \varphi \right) \epsilon^{A'_1 A'_2} \epsilon^{A'_2 A'_1} \\
 G'_1 &= H^0 \left( \frac{1}{\sqrt{A'_1}} \epsilon^{A'_1 A'_2} \cos^2 \varphi - \frac{1}{\sqrt{A'_2}} \epsilon^{A'_2 A'_1} \cos^2 \varphi \right) \cos \varphi \sin \varphi \\
 G'_2 &= -H^0 \left( \frac{1}{\sqrt{A'_1}} \epsilon^{A'_1 A'_2} \cos^2 \varphi - \frac{1}{\sqrt{A'_2}} \epsilon^{A'_2 A'_1} \cos^2 \varphi \right) \cos \varphi \sin \varphi
 \end{aligned} \quad (7-35)$$

According to Chap. 3 (b), the relative principal values  $A'_1$ ,  $A'_2$  are positive, therefore the decay constants  $\beta'_1$  and  $\beta'_2$  are certainly real. Because of the boundary condition at infinity, we must take them to be positive.

According to this, a noncubic crystal superconductor in a magnetic field also has a protecting layer under which exists a field-free region. In contrast to the case with a scalar  $\beta$ , the decay does not follow one exponential function but two. Furthermore, the magnetic field strength in the protecting layer does not have the same direction  $\epsilon_{A'_2}$  everywhere, as in the outside space, nor does the current density have the same direction  $\epsilon_{A'_1}$  everywhere perpendicular to this. Neither does the scalar product  $(I'_1, H)$  vanish. However, the two parts of the energy density, due to the supercurrent and due to the magnetic field, remain equal to each other, because from eq. 7-36

$$\frac{1}{2} (I'_1, 0) = \frac{1}{2} (0, H) \quad (7-37)$$

Also the total surface current  $\int d\sigma d\tau_3$  flows perpendicular to  $H^0$  and its value is defined exclusively by  $H^0$  through eq. 7-36:

$$\int d\sigma_1 d\tau_3 = c H^0, \quad \int d\sigma_2 d\tau_3 = 0 \quad (7-38)$$

This can of course be deduced directly from the Maxwell equations. All these differences vanish either if the relative principal values  $A'_1$  and  $A'_2$  are equal, or if the external field coincides in direction with one of the solutions 7-34 or 7-35. Then we return to

One might also apply this solution to slightly curved conductors in so far as they are thick compared with the penetration depths  $(A'_1)^{-1}$  and  $(A'_2)^{-1}$ , by considering the respective tangent planes as the  $\tau_3$  plane. For thin superconductors, however, the conditions are different. We see easily from eq. 7-33 that for a sufficiently thin plate the external magnetic field penetrates without hindrance and that a supercurrent is evenly distributed over it. From this we infer that the conclusions drawn in (1) for thin cubic crystal superconductors may also be applied to other lattices. As a confirmation of this we find in Chap. 8 (e) and Chap. 11 (C) that the solutions of London's equations, which lead to the above conclusions for cubic crystal cylinders and spheres, can under suitable conditions be applied to other crystal lattice forms.

<sup>11</sup>  $I'_3$  is generally not zero but  $I'_3 = \lambda_1 I'_1 + \lambda_2 I'_2$ .

### CHAPTER 8

#### The Current Flowing in a Wire

(a) In sections (a) to (d) we shall discuss a circular cylinder of radius  $R$  carrying a current  $J$  in the direction of its axis, the  $z$  axis. We assume the current to be confined to a coaxial cylindrical shell so that we shall have a well-defined axially symmetrical external field. We assume the material of the superconductor to have a homogeneous cubic crystalline structure. We use cylindrical coordinates, the distance  $r$  from the axis, the azimuth angle  $\theta$  measured in the axial direction, forming a right-handed system with  $z$  in the order  $r, \theta, z$  (compare Fig. 8-1). In these coordinates the components of the vector curl are

$$\text{curl}_r \mathbf{A} = \frac{1}{r} \frac{\partial A_\theta}{\partial \theta} - \frac{\partial A_r}{\partial z} \quad (8-1)$$

FIG. 8-1. Cylindrical coordinates  $r, \theta$  for a wire. The  $r$  axis is directed toward the reader;  $A$  is the intersection of the  $x$  axis with the plane of the diagram.

$$\text{curl}_\theta \mathbf{A} = \frac{\partial A_r}{\partial z} - \frac{\partial A_z}{\partial r} \quad (8-1)$$

$$\text{curl}_z \mathbf{A} = \frac{1}{r} \frac{\partial (r A_\theta)}{\partial r} - \frac{1}{r} \frac{\partial A_\theta}{\partial z} \quad (8-1)$$

$$\text{and for a scalar } u: \quad \frac{d u}{d r} = \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\partial u}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 u}{\partial \theta^2} + \frac{\partial^2 u}{\partial z^2} \quad (8-2)$$

In what follows we shall use solutions of the differential equation  $d u / d r - \beta^2 u = 0$  of the form

$$u = / (r) e^{i \theta} e^{i z} \quad (n \text{ an integer}) \quad (8-3)$$

Then  $/ (r)$  must satisfy the equation

$$\frac{1}{r} \frac{d}{d r} \left( r \frac{d /}{d r} \right) + \left( k^2 - \beta^2 - \frac{n^2}{r^2} \right) / = 0 \quad (8-4)$$

By the substitution  $x = / \sqrt{k^2 - \beta^2} r$  this is transformed into the Bessel equation

$$\frac{1}{x} \frac{d}{dx} \left( x \frac{d /}{d x} \right) + \left( 1 - \frac{n^2}{x^2} \right) / = 0 \quad (8-5)$$

The solutions of eq. 8-5 which remain finite for  $x = 0$  are the Bessel functions  $I_n(x)$ , namely,

$$\begin{aligned} I_0(x) &= 1 - \frac{(1/x)^4}{(1!)^4} + \frac{(1/x)^8}{(2!)^4} - \dots + \frac{(-1)^m (1/x)^{2m}}{(m!)^2} \dots \\ I_1(x) &= \frac{1/x}{0!1!} - \frac{(1/x)^5}{1!2!} + \frac{(1/x)^9}{2!3!} \dots - \frac{(-1)^m (1/x)^{2m+1}}{m!(m+1)!} \dots \\ I_2(x) &= \frac{(1/x)^4}{0!2!} - \frac{(1/x)^8}{1!3!} + \frac{(1/x)^{12}}{2!4!} \dots - \frac{(-1)^m (1/x)^{2m}}{(m+1)!} \dots \end{aligned} \quad (8-6)$$

One may verify that these series satisfy the following equations:

$$\begin{aligned} \frac{dI_0(x)}{dx} &= -I_1(x) & \int \hat{I}_{01}(z) dz = x I_1(x) \\ \frac{dI_1(x)}{dx} &= I_0(x) - \frac{1}{x} I_1(x) & \int \hat{z}^2 I_{01}(z) dz = x^2 I_1(x) \\ \frac{d}{dx} [x I_1(x)] &= I_0(x) & \int \frac{d}{dz} [x I_1(z)] dz = I_0(x) \\ \frac{d}{dx} [x I_0(x)] &= I_0(x) & I_0(x) + I_1(x) = \frac{2}{x} I_1(x) \end{aligned} \quad (8-7)$$

For real arguments  $x$  the functions  $I_n(x)$  oscillate about zero and have an infinity of roots. For pure imaginary arguments, the functions increase monotonically without limit with increasing argument.

(b) Let us consider an infinitely long homogeneous superconducting circular cylinder. By symmetry the current density is parallel to the axis and depends only on  $r$ . Therefore  $I_r$  must obey the differential eq. 8-4 with  $n = 0$  and  $k = 0$ . The substitution used in the transition to eq. 8-5 is now  $x = i\beta r$  and so

$$I_r = C I_0(i\beta r), \quad I_r = I_r = 0 \quad (8-8)$$

The integration constant is determined by the condition that a total current  $I$  flows through the cross section. Consequently,

$$I = 2\pi \int_0^R r I_r dr = 2\pi C \int_0^R r I_0(i\beta r) dr = 2\pi \frac{C R}{\beta} [-i I_1(i\beta R)] \quad (8-9)$$

(see eq. 8-7). From this it follows that

$$C = \frac{(I_1(i\beta R))^2 \pi R}{I_1(i\beta R)}, \quad I_r = \frac{i\beta I_1(i\beta R)}{2\pi R} \frac{I_0(i\beta R)}{I_1(i\beta R)} \quad (8-10)$$

In accordance to eq. 8-6  $I_0(i\beta R)$  is real and positive, while  $I_1(i\beta R)$  is positive imaginary, the right sides of these equations are positive real.

The magnetic field strength is determined by the fundamental eq. X:

$$\mathbf{H} = -\alpha \cdot \mathbf{curl} \mathbf{I} \quad (8-11)$$

Therefore according to eq. 8-1

$$\begin{aligned} \mathbf{H}_r &= \mathbf{H}_z = 0, & \mathbf{H}_\theta &= c \lambda \frac{\partial I_r}{\partial r} = i c \lambda \beta C \left( \frac{dI_0(i\beta R)}{dr} \right) \dots, \\ \text{that is by eqs. 8-7 and 6-7:} \quad \mathbf{H}_\theta &= \sqrt{\lambda C} [-i I_1(i\beta R)] = \frac{I}{2\pi R} \frac{I_0(i\beta R)}{I_1(i\beta R)} \end{aligned} \quad (8-10) \quad (8-11)$$

We can check this equation by setting  $r = R$ . At the surface of the cylinder carrying a total current  $I$  we must have

$$\mathbf{H}_\theta = \frac{I}{2\pi R} \quad (8-12)$$

and this actually is the result.

The Bessel functions  $I_m(x)$  and  $I_m(x)$  increase toward infinity as  $x^2/2$ . If  $\beta R$  is a high number, the wire therefore becomes thick compared with the penetration depth, then according to eq. 8-3 with  $\beta r \gg 1$ ,  $I_r$  contains the factor  $e^{-i\beta r}$ . The current, and likewise the magnetic field, lie almost entirely in a protecting layer of thickness  $\beta^{-1}$ . On the other hand  $I_0(i\beta R)$  has a minimum at  $x = 0$  (equal to 1), and if  $\beta R \ll 1$ , then the current density  $I_r$  increases only slightly from the axis to the perimeter — it is more or less evenly distributed over the section. Both results were to have been expected according to Chap. 7.

(c) Now let the cylinder consist of a normally conducting part where  $r < 0$  and a superconducting part where  $r > 0$ . According to Chap. 7 the electrostatic potential is constant inside the superconductor. The boundary plane at  $r = 0$  is thus an equipotential surface for the normal conductor; therefore the current flows exactly as in a wire of unlimited length, namely, it is evenly distributed over the cross section. The current density is

$$I_r = \frac{I}{\pi R^2} \quad (z < 0) \quad (8-13)$$

The magnetic lines of force here are circles around the axis of the wire. Since  $\mathbf{H}_\theta$  is integrated round a circle of radius  $r < R$  must equal the total current through the circle,  $I_r \pi R^2$ , divided by  $c$ , we have

$$\mathbf{H}_\theta = \frac{r^2 I_r}{2\pi R^2} \quad (z < 0) \quad (8-14)$$

On entering the superconductor the current must restrict itself to the boundary layers. We have therefore to take into account a radial component  $I_r$  in the neighborhood of the boundary plane. Because of this it is more expedient to start with the magnetic field strength which even at this point has by symmetry only a component  $H_z$  independent of  $0$ . For large positive values of  $r$  we can use the solution 8-11 directly; in the neighborhood of  $r = 0$ , however, other terms have to be added that decrease with increasing  $r$ .

As already mentioned, the differential equation  $\partial u / \partial^2 u = 0$  holds for  $H_x$  and  $H_y$ , but not for  $H_\theta$  which is associated with a curvilinear coordinate. Since, however,

$$\begin{aligned} H_x &= -H_y \sin \theta, & H_y &= H_x \cos \theta, \\ H_\theta &= -i H_x / (r e^{-i\beta r}) \sqrt{1 + \beta^2 r^2}, \end{aligned}$$

so that we get

$$H_x = -i H_\theta \sin \theta, \quad H_y = i H_\theta \cos \theta,$$

Comparison with eq. 8-3 proves that  $I/r$  must be a solution of eq. 8-4 with  $n = 1$  and  $k = \sqrt{\alpha_0^2 + \beta^2}$ , i. e.,

If we insert such additional terms  $I(r)/r = I_1(\alpha_0 r)$  in the solution 8-11 it becomes inconsistent with eq. 8-12, an equation that must still hold, we therefore determine  $\alpha_0$  by the requirement that

$$I_1(\alpha_0 R) = 0 \quad (8-14)$$

As there are infinitely many zeros of  $I_1(z)$ , a discrete but infinite set of real  $\alpha_0$  values satisfy this condition.

In this way we arrive at the following series for  $H_\theta$ :

$$H_\theta = \frac{I}{2\pi c R} \left[ \frac{I_1(\beta R)}{I_1(i\beta R)} + \sum_{p=1}^{\infty} a_p I_1(\alpha_p r) e^{-i\beta p \theta} \right] (x > 0) \quad (8-15)$$

and now have only the coefficients  $a_p$  to calculate. For this purpose the continuity condition for  $H_\theta$  at  $x = 0$  is available.

$$\sum_{p=1}^{\infty} a_p I_1(\alpha_p r) = \frac{r}{R} - \frac{I_1(i\beta R)}{I_1(i\beta R)} \quad (8-16)$$

must hold identically in  $r$ . To carry out the calculations two relations are available which we accept without proof:

$$\int_0^R r I_1(\gamma r) I_1(\delta r) dr = \frac{[AR I_1(\gamma R) I_0(\delta R) - \gamma R I_1(\delta R) I_0(\gamma R)]}{(\gamma^2 - \delta^2)} \quad (8-17)$$

$$\int_0^R r I_1^*(\gamma r) dr = \frac{1}{2} R^2 [I_1^*(\gamma R) - I_0(\gamma R) I_1(\gamma R)] \quad (8-17)$$

From the first of these follows the important fact that the functions  $I_1(\alpha_p r)$  selected by eq. 8-14 form an orthogonal system, i. e.,

$$\int_0^R r I_1(\alpha_p r) I_1(\alpha_q r) dr = 0 \quad \text{for } \alpha_p \neq \alpha_q$$

Multiplying eq. 8-16 by  $r I_1^*(\alpha_p r)$  and integrating from 0 to  $R$  therefore eliminates all the coefficients except  $a_p$  and yields for the value

$$a_p = \frac{\int_0^R \left[ \frac{r}{R} - \frac{I_1(i\beta R)}{I_1(i\beta R)} \right] I_1(\alpha_p r) dr}{\int_0^R r I_1^*(\alpha_p r) dr} \quad (8-18)$$

The integration can be carried out easily by means of eqs. 8-7 and 8-17. The result is

The thinner the wire the greater become the  $\alpha_p$  and if  $\beta R \ll 1$ , they then all decrease, and with them the sum in eq. 8-19, and so also the radial

$$a_p = -\frac{1}{2\alpha_p R} \left\{ \frac{1}{I_0(\alpha_p R)} + \frac{\alpha_p^2 / (\alpha_p^2 + \beta^2)}{I_1(\alpha_p R)} \right\} \quad (8-18)$$

Because of the last of the equations 8-7, eq. 8-14 is  $I_1(\alpha_p R) = -I_0(\alpha_p R)$  so

$$a_p = -\frac{1}{2\alpha_p R} \frac{\beta^2 / (\alpha_p^2 + \beta^2)}{I_0(\alpha_p R)}. \quad (8-18)$$

We get the current density now from the fundamental eq. 11:

$$I = r \operatorname{curl} H_\parallel \quad (8-18)$$

According to eqs. 8-1, 8-7, and 8-15 this yields

$$I_p = -c \frac{\partial H_\theta}{\partial z} = \frac{I}{2\pi c R} \sum_{p=1}^{\infty} a_p I_1(\alpha_p r) e^{-i\beta p \theta}, \quad (8-19)$$

$$I_p = \frac{c}{2\pi c R} \frac{d(I_p H_\theta)}{dr} + \sum_{p=1}^{\infty} a_p \alpha_p I_1(\alpha_p r) e^{-i\beta p \theta}. \quad (8-19)$$

Because of eq. 8-14,  $I_p$  vanishes at the surface of the cylinder  $r = R$  as required. The same is true at  $r = 0$  because  $I_1(0) = 0$ .

Furthermore, as soon as  $\beta \gg 1$ , both  $I_p$  and that part of  $I_p$  represented by the sum over  $p$  vanish. Then  $I_p$  assumes the same value as for the infinitely long superconducting cylinder given in eq. 8-9. The transition to the even current distribution that still exists at the boundary  $r = 0$  distance  $\beta^{-1}$ , the distribution that characterizes the superconductor is effected in a

The first roots of eq. 8-14 are

$$a_1 R = 3.85, \quad a_2 R = 7.02, \quad a_3 R = 10.2, \quad a_4 R = 16.6 \dots$$

If therefore  $\beta R \gtrsim 100$  (with  $\beta = 10^5 \text{ cm}^{-1}$ ,  $R = 10^{-3} \text{ cm}$ ) is sufficient for this), these first  $a_p$  are all small compared with  $\beta$ . But according to what has been said in section (b) about the exponential decay of the first terms, this contribution to  $I_p$  is practically the only one in the region where  $r$  is considerably smaller than  $R$ . So in this region the lines of flow, which leave the boundary of the normal conductor evenly distributed and perpendicular to the boundary, bend sharply into the radial direction. They have to do this because the major portion of the current must be deflected from the interior of the wire into the protecting layer of thickness  $\beta^{-1}$  adjoining the cylinder's surface, and do this within a distance of  $\beta^{-1}$  in the  $z$  direction.

The thinner the wire the greater become the  $a_p$ . According to eqs. 8-18 the coefficients  $a_p$  are considerably greater than  $\beta$ . According to eq. 8-19 the coefficients  $a_p$

current  $I_r$ . The latter is no longer needed because, according to (6) the current is uniformly distributed over the cross section even in the superconductor.

(d) Let the cylinder now consist of two superconductors touching in the plane  $x = 0$ , let the poorer superconductor lie below this plane:  $z < 0$ , corresponding to the smaller angle  $\lambda'$ , and therefore to the reciprocal penetration depth  $\beta'$ . By section (b) the current distribution depends on  $\beta$  so transition phenomena must now appear on both sides of the boundary.

For  $z > 0$  we can retain the expression 8-15 with the values of  $a_p$  given by eq. 8-14, and also the consequent eq. 8-19. For  $z < 0$  we write down the analogous expression:

$$H_{\theta'} = \frac{I}{2\pi R} \left[ \frac{I_1(\mu\beta)}{\mu_1(\mu\beta R)} + \sum_{p=1}^{\infty} a_p' I_1(a_p r) e^{+i\sqrt{\alpha_p^2 + \beta'^2}r} \right] \quad (z < 0) \quad (8-20)$$

The resulting calculation of the current distribution differs from eq. 8-19 not only in the sign of the exponents but also in the signs of the right-hand side of the equations for  $I_r$ . We have two boundary conditions to evaluate the coefficients  $a_p$  and  $a_p'$ , first the continuity of  $H_{\theta}$  and second (see Chap. 3-9)

$$I_r = \lambda' I_r' \quad (8-21)$$

according to eq. 6-7 we can also write for this

$$\frac{I_r}{I_r'} = \frac{\beta^2}{\beta'^2} \quad (8-22)$$

This second condition is fulfilled identically in  $r$  only if the corresponding coefficients in the two series for  $I_r$  and  $I_r'$  are in the ratio  $\beta^2/\beta'^2$ :

$$\frac{a_p}{a_p'} \sqrt{\frac{(\alpha_p^2 + \beta^2)}{(\alpha_p^2 + \beta'^2)}} = -\frac{\beta^2}{\beta'^2} \quad (8-23)$$

$$\text{or} \quad a_p' = -a_p \left( \frac{\beta'}{\beta} \right)^2 \sqrt{\frac{(\alpha_p^2 + \beta^2)}{(\alpha_p^2 + \beta'^2)}} \quad (8-24)$$

The continuity of  $H_{\theta}$ , however, requires that

$$\sum_{p=1}^{\infty} (a_p - a_p') I_1(a_p r) = \frac{I_1(\mu\beta r)}{\mu_1(\mu\beta R)} - \frac{I_1(\lambda'\beta r)}{\lambda'_1(\lambda'\beta R)} \quad (8-25)$$

identically in  $r$ . Applying the method used in (b) we conclude:

$$a_p - a_p' = \frac{2 a_p}{R T_0 (\mu_r R) \sqrt{(\alpha_p^2 + \beta^2)(\alpha_p^2 + \beta'^2)}} \quad (8-26)$$

This equation and 8-24 determine both  $a_p$  and  $a_p'$ . We see that if we assume  $\beta' = \beta$  all the  $a_p$  and the  $a_p'$  vanish, as indeed must be so.

The transformation from one current distribution to the other takes place in two layers adjoining the boundary plane  $z = 0$  of thickness  $\beta^{-1}$

## 8. CURRENT FLOWING IN A WIRE

and  $\beta'^{-1}$  respectively. It is effected by radial currents in both superconductors. To find the contributions of each of the two conductors, we compare the integrals  $\int_i ds$  and  $\int_{i'} ds$ . As

$$i_r = -c \frac{\partial H_{\theta}}{\partial z} \quad (8-27)$$

both yield the same value for  $(H_{\theta})_{z=0}$ . The greater absolute value of  $i_r$  which according to eq. 8-21 occurs in the better superconductor, is compensated by the smaller depth of the boundary layer. In the three cases treated here the magnetic field outside the superconductor is known *a priori*. The solutions therefore come under the uniqueness theorem of

Chap. 7 (a).

(d) The solutions of section (b), i. e., of the problem of the infinitely long cylinder carrying a current, can be applied to noncubic crystal superconductors only if one of the axes of the ellipsoid representing the tensor  $A_{\mu\nu}$  coincides with the axis of the cylinder. We call this axis the  $x_3$  axis. If  $i_r$  has this direction everywhere then by eq. VIII-7 the supercurrent calculation has only one component  $Q_3$ . The only tensor component that enters the calculation is the principal value  $A_3$ . It is only necessary to replace  $\beta$  in eqs. 8-9 and 8-10 by

$$A_3 = \frac{1}{c\sqrt{A_3}} \quad (8-28)$$

to take over the former solution. Its uniqueness is again guaranteed by the theorem of Chap. 7 (a).

(f) It has not yet been possible to give a rigorous solution of our problem for a cylinder with an elliptical cross section except in the approximation corresponding to the "thick" cylinder. In this case the circumference of the surface is a line of force of the external magnetic field. This field is irrotational and its potential obeys the equation  $\nabla^2 \phi = 0$ , but it increases with each turn around the cylinder by the "period"

$$-\oint H \cdot d\hat{s} = -\frac{I}{c} \quad (8-29)$$

where, as before,  $I$  means the total current in the cylinder. Let the axes of the elliptical cross section be  $a$  and  $b$  ( $a > b$ ). The "thick" cylinder is characterized by the fact that the smallest radius of curvature  $R_{min}$  at the ends of the greater axis is great compared with the penetration depth  $\beta^{-1}$ . The same holds *a fortiori* for  $b$ .

It is well known that if a functional relation  $\zeta = f(x)$  exists between two complex variables  $\zeta = x + iy$  and  $\zeta = \psi + i\varphi$ , then  $y$  and  $\varphi$  are solutions of the potential equation. In the present problem

$$\zeta = C \cos(i\varphi) = C [\cosh(a\psi) \cos(a\varphi) + i \sinh(a\psi) \sin(a\varphi)] \quad (8-26)$$

can be adjusted to the given boundary conditions. The constants  $C$  and  $a$  are available for this purpose.

Thus it follows from eq. 8-26 that

$$x = C \cosh(\alpha y) \cos(\alpha \varphi), \quad y = C \sinh(\alpha y) \sin(\alpha \varphi) \quad (8-27)$$

Elimination of  $\varphi$  yields

$$\left[ \frac{x}{\cosh(\alpha y)} \right]^2 + \left[ \frac{y}{\sinh(\alpha y)} \right]^2 = C^2 \quad (8-28)$$

The curves  $y = \text{constant}$  are everywhere orthogonal to the curves  $\varphi = \text{constant}$  and so represent the lines of force. If we fix a value  $\psi_0$  in such a way that

$$a = C \cosh(\alpha \psi_0) \quad \text{and} \quad b = C \sinh(\alpha \psi_0)$$

or

$$C^2 = a^2 - b^2, \quad \tanh(\alpha \psi_0) = \frac{b}{a} \quad (8-29)$$

then the surface of the cylinder contains the corresponding line of force required by the one boundary condition. All the other lines of force ellipses confoal with the cross section of the cylinder. The period of the potential has the prescribed value if we put

$$a = -\frac{2\pi c}{f}, \quad b = \frac{2\pi c}{f} \quad (8-30)$$

The magnitude  $H$  of the field strength follows from the general equation according to eq. 8-26:

$$H = \frac{1}{|C| |\sinh(\alpha y)|} |dz/dx|$$

$$= \frac{1}{\{C |a| [\sinh^2(a y) \cos^2(\alpha y) + \cosh^2(\alpha y)]\}^{1/2}} \quad (8-31)$$

In particular the field strength at the surface  $y = \psi_0$  is (see eq. 8-29)

$$H^0 = \frac{f}{2\pi c} \{a^2 \sin^2(\alpha y) + b^2 \cos^2(\alpha y)\}^{-1/2} \quad (8-32)$$

Consequently at the end point of the greater axis ( $y = 0$ ,  $\sin(\alpha y) = 0$ ,  $\cosh(\alpha y) = 1$ ),  $H^0$  is a maximum exceeding the minimum at the end of

<sup>1</sup>The transformation from  $\varphi$  to the polar angle  $\theta = \arctan y/x$  can be effected by an equation following from eq. 8-27:

$$\tan \theta = \tanh(\alpha y) \tan(\alpha \varphi)$$

Applying this to eq. 8-32 we have to put  $\tan \theta = (b/a) \tan(\alpha \varphi)$  according to eq. 8-29. The result is

$$H^0 = \frac{f}{2\pi c} \sqrt{\frac{(a^2 \sin^2 \theta + b^2 \cos^2 \theta)}{(a^2 \sin^2 \theta + b^2 \cos^2 \theta)}}$$

the smaller axis ( $x = 0$  and  $\cos(\alpha y) = 0$ ) by the factor  $a/b$ . According to eq. 7-38 this statement is equally true of the surface density of the supercurrent, whatever the crystal structure of the conductor. If  $d$  is the perpendicular distance of an interior point from the surface, then according to eq. 7-10 for a cubic lattice, the current density within the protecting layer is

$$i_s = H^0 \lambda^{-3/2} e^{-\rho d} \quad (8-33)$$

and practically no current is flowing in the protected region beneath.

(g) The fact that the supercurrent prefers protruding edges is no peculiarity of the elliptical cylinder, but a general characteristic of this current. It is caused by the well-known fact that when the lines of force envelope the surface of a body, the field intensity is considerably increased at such edges. The potential theory proves this as follows.

If as in section (f) we start from the conformal mapping  $\chi = -iC \zeta^n$  then we, the real part of  $\chi$ , equals  $C [\zeta^n \sin(\theta + \phi)]$ , we take  $n > 1$  to be a fraction between  $1/2$  and  $1$ . The line of force  $y = 0$  consists of the radial lines  $\theta = 0$  and  $\theta = \pi/n$ . In our mapping we see the representation of a field whose lines of force run along the surface of the superconductor filling the space  $\pi/n < \theta < 2\pi$ . At the protruding edge  $\zeta = 0$

$$H = \left| \frac{dz}{d\zeta} \right| = n C |\zeta|^{n-1}$$

becomes infinite. If the edge is not mathematically sharp, but rounded,  $H$  remains finite, but in any case becomes especially large compared with the surrounding field. If we choose  $n > 1$  we get a re-entrant edge and see that  $H$  decreases to zero therein.

In a column with rectangular cross section the strongest current runs along the four edges.

However this holds only under the conditions for a "thick" superconductor, and this excludes mean radii of curvature comparable with or smaller than the penetration depth  $\beta^{-1}$ . In extremely thin superconductors the supercurrent is distributed evenly over the cross section in accordance with Chap. 7 (g).

## CHAPTER 9

## The Current Flowing in a Hollow Cylinder

(a) For our present discussion let us consider a hollow cylinder with inner radius  $R_i$  and outer radius  $R_o$ . Let the cylinder be homogeneous, superconducting, and have cubic crystal structure; let a total current  $I$  flow along it. But also let a wire, either normal or superconducting, be placed along the axis of the cylinder and carry another current  $I'$ . We consider  $I$  or  $I'$  to be positive if they flow in the positive  $x$  direction. Imagine the circuit to be closed by means of a coaxial cylindrical shell at infinity, as in Chap. 8.

Under these circumstances the magnetic field strength at the inner cylindrical surface  $r = R_i$  is

$$H_0 = \frac{I'}{2\pi c R_i} \quad (r = R_i) \quad (9-1)$$

because a circle of radius  $R_i$  encloses the current  $I'$ . A circle lying in the outer cylindrical surface ( $r = R_o$ ), however, encloses the total current  $I + I'$ . Consequently the field strength there is

$$H_0 = \frac{I + I'}{2\pi c R_o} \quad (r = R_o) \quad (9-2)$$

From these conditions we can obtain the fields within the cylinder uniquely according to the theorem of Chap. 7 (a).

The current is parallel to  $x$  and depends only on  $r$  just as for the solid cylinder (Chap. 8 [6]). Furthermore  $I_0$  is again a solution of the differential equation  $d^2u - \beta^2 u = 0$ . But Eq. 8-8 is insufficient because we cannot satisfy both conditions 9-1 and 9-2 with only one integration constant. However, we are relieved of the requirement that  $I_0$  must remain finite for  $r = 0$  because the domain of the desired solution does not extend so far. Therefore we can generalize the expression 8-8 as follows:

$$I_0 = C f_0(\beta r) + D H_0(\beta r) \quad (9-3)$$

where  $H_0(x)$  is the Hankel function of the first kind and zero order, namely, that solution of the differential eq. 8-5 with  $n = 1$ .  $H_1(x)$  is negative logarithmically infinite at the origin,  $f_0(x)$  also satisfies eq. 8-5 with  $n = 0$  which becomes so defined that  $f_0'(x)$  is positive real for positive  $x$  and behaves like  $-1/(2\pi c) \ln x$ ; it decreases monotonically with increasing  $x$ , and finally vanishes asymptotically. The Hankel function of the first kind and first order  $H_1(x)$  is connected with  $H_0(x)$  by the relation

<sup>1</sup>We can omit the usual superscript 1 because we shall not have to deal with the Hankel function of the second kind.

$$\frac{dH_0(x)}{dx} = -H_1(x) \quad (9-4)$$

and is a solution of the differential eq. 8-5 with  $n = 1$ .  $H_1(x)$  is negative real everywhere, becoming infinite like  $-2/(c\pi x)$ ; it increases monotonically reaching the value zero only for infinitely large positive values of  $x$ . It now follows from eq. 8-10 that

$$H_0 = c \cdot \frac{\partial i_1}{\partial r} = \sqrt{\hat{V}} [C - I_1(i\beta r) + D H_1(i\beta r)] \quad (9-5)$$

According to eqs. 9-1 and 9-2, the equations determining the constants  $C$  and  $D$  are

$$-C I_1(i\beta R_i) + D H_1(i\beta R_i) = \frac{\beta}{2\pi R_i} I' \quad (9-6)$$

$$\rightarrow -C I_1(i\beta R_i) + D H_1(i\beta R_i) = \beta(I' + I') \quad (9-6)$$

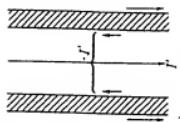
We need not write out the solution explicitly. For a thick hollow cylinder, i.e., when  $R_o - R_i \gg \beta^{-1}$ , the first terms in eqs. 9-3 and 9-5 decrease toward the interior and can be neglected completely in the neighborhood of  $R_i$ , and similarly the second terms decrease toward the outside and are negligible near  $R_o$ .

Then we have simply

$$C = \frac{(I + I')(c/2\pi R_i)}{I_1(i\beta R_i)}, \quad D = \frac{I'(j\beta/\pi R_i)}{H_1(i\beta R_i)} \quad (9-7)$$

Comparing this value of  $C$  with that in eq. 8-9 we see that the outer protecting layer of the cylindrical shell now carries the current  $\hat{I}' + I'$ . The equation for  $D$  shows that the protecting layer adjoining the inner surface carries the current  $-I'$  because  $H_1(i\beta R_i)$  is negative. (See Fig. 9-1.) And this must be true because a circle  $r = \text{constant}$  within the protected interior of the cylindrical shell must enclose zero net current, because  $H = 0$  on the circle. This current  $\hat{I}'$  on the inner wall of the shell must be compensated by an additional current  $-I'$  in the outer cylinder;  $I'$  is the current in the coaxial wire.

Fig. 9-1. Current distribution in a hollow superconducting cylinder with a coaxial wire. The outer current  $\hat{I}'$  is the net current in the superconducting cylinder. The inner current  $I'$  is the current in the coaxial wire. The outer current  $\hat{I}'$  on the inner wall of the shell must be compensated by an additional current  $-I'$  in the outer cylinder;  $I'$  is the current in the coaxial wire. Also it is only in this way that we can satisfy at the inner wall the rule that the current, the magnetic field strength, and the inner normal to the superconductor form a right-handed system. For thin hollow cylinders,  $R_o - R_i \ll \beta^{-1}$ , one develops the two cylinder functions of eq. 9-9 in powers of  $r - R_i$ , starting from  $R_o = \nu_j(R + R_i)$ . One sees without calculation that, to a first approximation there is a linear transition from one to the other of the two values of  $H_0$  prescribed by eqs. 9-1 and 9-2. This corresponds to the linear transition in the thin plane parallel plate of Chap. 7, eq. 7-17.



$\hat{I}' + I'$

The solution given in eqs. 9-6 and 9-7 can be generalized to non-crystalline as in Chap. 8 (e) if one principal axis of the tensor fails in the direction of the cylinder. One only has to replace  $\beta$  by the  $A_0$  of eq. 8-25. Everything that follows in this chapter holds independently of all crystallographic properties.

As explained in Chap. 1 every "thick" superconductor (there have been scarcely any experiments done on thin hollow cylinders) can stand only a certain critical value  $H_{c2}$  of its surface. According to eqs. 9-1 and 9-2 this sets a limit for the superconducting state of the hollow cylinder:

$$|I'| < 2\pi e R_1 H_{c2}, \quad |I + I'| < 2\pi e R_1 H_{c2}.$$

If we plot  $I$  and  $I'$  as coordinates in a plane (Fig. 9-2) the interior of the shaded parallelogram represents the region of superconductivity. This simple consequence of the Slabbe hypothesis has never been checked experimentally in a rigorous manner.

(b) Figure 9-3 represents the cross section of an arrangement of normal and superconducting parts symmetric with respect to the  $x$  axis. Leads in the  $x$  axis carry the net current  $I$ . We ask what part of  $I$  flows through the inner solid cylinder, and what part flows not in the superconductor, but in the normal conductor. The circular sections  $K$  and the annular ring  $R$  in the figure have the same potential because the electrostatic potential in a superconductor is constant. Potential theory applied to the interior of the normal conductor then tells us what part of  $I$  takes the path through the inner cylinder.

This current enters the superconductor at  $K$  and must finally reach the lower lead. As it cannot penetrate deeply into the superconductor, it can only go along the boundary of the superconductor, as sketched in the figure. It flows, in fact, across the plane  $K$  and there joins the current  $I - I'$  that enters the outer surface of the superconductor from above. The full current then flows down the outer surface to the lower leads.

The uniqueness of the solution sketched here is again guaranteed by the theorem of Chap. 7 (a). To begin with, owing to the symmetry of the arrangement, the magnetic field is known for all boundaries between normal and superconducting parts of a cylinder.

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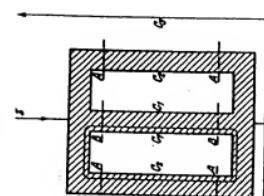


Fig. 9-4. Doubly connected superconductor in the same arrangement as in Fig. 9-3.

(c) Figure 9-4 represents a similar arrangement, only in this case the whole shaded area is to be superconducting. Again we imagine the current  $I$  to be fed in at  $Z = 0$  and carried back by a third cylinder  $C_3$  coaxial with  $C_1$  and  $C_2$ . This shields the field from outside. Because a curve enclosing it encloses a net current zero. The circuit for the current  $I$ , flowing in  $C_1$ , is completed by the inner walls of  $C_3$  and the two superconducting parts. It does not affect the outside at all, so long as the superconducting parts are thick compared with the penetration depth, but neither can it be influenced from the outside. It is a persistent current in what is here actually a doubly connected body. Its energy is substantially magnetic in nature and is located in the hollow space between  $C_1$  and  $C_2$  and has the form  $\alpha I_1^2$ ; the value of the constant  $\alpha$  is of no importance.

One can also consider this apparatus from another point of view. The parts formed by sections at  $A$  and  $B$  can be regarded as superconductors in parallel in the sense of Chap. 2. In order to permit the current strength  $I_1$  in the cylinder  $C_1$  a current  $I - I_1$  must flow along its outer walls because the inner wall carries the current  $I - I_1$ . Consequently the energy located between  $C_1$  and  $C_3$  (and to an unimportant degree also in the protecting layer of  $C_3$ ) is of the form  $\gamma(I_1 + I_2)^2$ . Writing the total energy  $\rho_0 I_1^2 + \gamma(I_1 + I_2)^2$  in the form  $\frac{1}{2}(\rho_{11}I_1^2 + \rho_{22}I_2^2 + 2\rho_{12}I_1 I_2)$  we have  $\rho_{12} = \rho_{21} = \rho_{AB}$ . According to eq. 9-6 it follows that if there were no current in the system initially,  $I_1$  would remain zero after switching on the current  $I$ , while any initial current  $I_1$  would remain unchanged by switching on  $I$ .

These considerations, although leading to no new results, nevertheless show the intimate relations between the discussion of Chap. 2 and the theory explained in Chap. 3 and later chapters.

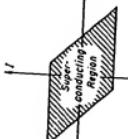


Fig. 9-5. Current distribution at the boundaries between normal and superconducting parts of a cylinder.

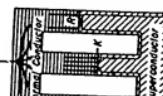


Fig. 9-6. Doubly connected superconductor in the same arrangement as in Fig. 9-3.

The requirements that  $H_z$  goes over continuously into  $H_r$  at  $r = R_i$  and to  $H_r$  at  $r = R_o$  serve to determine the constants  $C$  and  $D$ .

If the walls of the cylinder are thick compared with  $\beta^{-1}$  we can in eq. 10-4 neglect the first term when  $r = R_i$  and with  $\beta^{-1}$  we can in  $r = R_o$ , as we did in Chap. 9 (a). We then have to put

$$H_z = T_0(\beta r), \quad D = \frac{H_r}{T_0(\beta R)} \quad (10-6)$$

This leads back to eq. 10-1 for the layer at the outer boundary, while for the neighborhood of the inner boundary it follows that

$$H_z = H_r \frac{T_0(\beta r)}{T_0(\beta R)}, \quad I_r = -H_r \frac{\partial}{\partial r} T_0(\beta r) \quad (10-7)$$

Since  $H_r(\beta r)$  is negative while  $T_0(\beta r)$  is positive, the current for positive values of  $r$  in the field-free region has again the direction of increasing  $r$ . Between the two protective layers where these equations hold, let us choose  $H_r = 0$  if we ascribe to the cylinder a finite length which, however, is great compared with its diameter. eqs. 10-7 are still valid except in the neighborhood of the ends. Here we have an example of a persistent current, because indeed a hollow cylinder is a doubly connected body.

Let us assume the cylinder to be thin ( $R_o - R_i \ll \beta^{-1}$ ) and choose  $H_r = H_r$ . Writing  $R_m$  for the arithmetic mean between  $R_i$  and  $R_o$ , the first terms of the expansion will now suffice:

$$H_z = (H_r)_m + \left( \frac{\partial H_r}{\partial r} \right)_m (r - R_m) \quad (10-8)$$

If the right-hand side has to assume the same value,  $H_r$  at  $r = R_i$ , i.e., at  $r - R_i = -\frac{1}{2}(R_o - R_i)$ , as it does at  $r = R_o$ , i.e., at  $r - R_o = \frac{1}{2}(R_o - R_i)$ , then  $(\partial H_r / \partial r)_m$  must be zero; consequently according to eq. 10-5  $(I_r)_m$  is also zero. This again confirms the general argument of Chap. 7 (b) for thin specimens.

The validity given in eqs. 10-1 and  $10-2$ ,  $10-4$  and  $10-5$  remain valid for noncubic crystals provided the ellipsoid of the tensor  $A_{\mu\nu}$  has an axis of symmetry (say  $A_{33}$ ) in the direction of the axis of the cylinder, and the two principal values  $A_1$  and  $A_3$  coincide. Then for this problem the supermomentum is in fact always in the same direction as the supercurrent, just as in the cubic case, while

$$\beta_1 = \frac{1}{e^2 / J_1} \quad (10-8)$$

This becomes identical with eq. 7-29 if one puts  $L = R$  and  $r_i = r_o = \beta^{-1}R$ ; from the form of these two Bessel functions, discussed in Chap. 8 (b), it also follows here that the influence of the field on a thick wire is confined to a protecting layer of thickness  $\beta^{-1}0$  when  $H_r$  is positive because  $-I'_1(\beta r)$  is positive. This corresponds to the rule that current, field strength, and inner normal to the superconductor — here the negative  $r$  direction — form a right handed system. For a thin wire ( $R \ll 1$ ) the flat minimum of  $I'_0(\beta r)$  at  $r = 0$  shows that the field penetrates almost without loss. In this case

$$I_r = -\frac{1}{2} \frac{H^0 R^2}{T_0^2(\beta R)} \quad (10-3)$$

This becomes identical with eq. 7-29 if one puts  $L = R$  and  $r_i = r_o = \beta^{-1}R$ ; from this it follows, as in (a) (compare also eq. 9-5) that

$$I_r = -c \frac{\partial H_r}{\partial r} = c \beta C I_r(\beta r) - c \beta D H_r(\beta r) \quad (10-5)$$

## CHAPTER 10

### The Cylinder in a Homogeneous Magnetic Field

(a) We now place a homogeneous superconducting cylinder in a longitudinal magnetic field, no current flows in the direction of its axis; the external field has everywhere the same strength  $H_r = H$  outside the surface of the cylinder. In the interior of the cylinder  $H_r$  has to satisfy the equation  $dA/dx = 0$ , and must moreover depend only on the distance  $r$  from the axis. Like  $A_x$  current density  $I_r$  in Chap. 8 (b) which satisfied the same conditions,  $H_r$  must therefore be proportional to  $I_r(\beta r)$ . The boundary condition that  $H_r$  be continuous is then obviously satisfied by

$$H_r = H^0 \frac{I_r}{I_0(\beta R)} I_r(\beta r) \quad (10-1)$$

We find the current density from  $I_r = \epsilon \mathbf{A} \cdot \mathbf{curl} \mathbf{H}$ . According to eq. 8-1 this reads:

$$I_r = I_0 = 0, \quad I_r = -c \frac{\partial H_r}{\partial r} = c H^0 \frac{I_r}{I_0(\beta R)} \frac{d}{dr} \frac{I_r}{I_0(\beta R)} \quad (10-2)$$

From eq. 8-7  $dI_r / dr = -I'_1(x)$ . From the form of these two Bessel functions, discussed in Chap. 8 (b), it also follows here that the influence of the field on a thick wire is confined to a protecting layer of thickness  $\beta^{-1}0$ . The currents that provide this protection flow in the direction of increasing  $r$  when  $H_r$  is positive because  $-I'_1(\beta r)$  is positive. This corresponds to the rule that current, field strength, and inner normal to the superconductor — here the negative  $r$  direction — form a right handed system. For a thin wire ( $R \ll 1$ ) the flat minimum of  $I'_0(\beta r)$  at  $r = 0$  shows that the field penetrates almost without loss. In this case

$$I_r = -\frac{1}{2} \frac{H^0 R^2}{T_0^2(\beta R)} \quad (10-3)$$

This becomes identical with eq. 7-29 if one puts  $L = R$  and  $r_i = r_o = \beta^{-1}R$ , and strength  $H_r = H_r$  in the bore, whereas outside there is a homogeneous differential equation as in case (a); but for the reasons we have discussed in Chap. 9 (a) in connection with the hollow cylinder carrying a current, we now write down the analogous expression to eq. 9-3:

$$H_r = C I'_0(\beta r) + D H'_0(\beta r) \quad (10-4)$$

From this it follows, as in (a) (compare also eq. 9-5) that

$$I_r = -c \frac{\partial H_r}{\partial r} = c \beta C I_r(\beta r) - c \beta D H_r(\beta r) \quad (10-5)$$

$$(10-8)$$

(c) Now let us imagine a solid cylinder of radius  $R$  with no longitudinal current, placed in a field perpendicular to its axis — a transverse field. The field does not remain homogeneous as the lines of force must go around the cylinder if the latter is not too thin, i. e., they are deflected by it as shown in Fig. 1-5. If we substitute with the approximation used in the figure, which regards the superconductor as completely impermeable to the field (a case for which the distortion of the field can easily be

calculated by potential theory) we have to try to determine the internal and the external field simultaneously. We come here for the first time to an uniqueness theorem of Chap. 7 (a) is no longer applicable; instead we shall meet a more general uniqueness theorem worked out in Chap. 12 (d).

To supplement the polar coordinate  $r$  and  $\theta$  used hitherto:

$$x = r \cos \theta, \quad y = r \sin \theta.$$

Suppose the intensity of the homogeneous field has the positive direction and magnitude  $H_0$ . Its potential would then be

$$\Phi = -H_0 x = -H_0 r \cos \theta$$

According to potential theory a completely impenetrable cylinder would act at points outside it as a dipole sheet, and its potential would be of the form  $(a'/r) \cos \theta$ , with  $a' = R^2$ . We therefore seek a rigorous solution of the problem in the following form with  $a$  at first undetermined:

$$\Phi = -H_0 \left( r + \frac{a}{r} \right) \cos \theta \quad (10-9)$$

Because  $H = -\nabla \Phi$  it follows that

$$H_x = -\frac{\partial \Phi}{r \partial \theta} = H_0 \left( 1 + \frac{a}{r^2} \right) \cos \theta$$

(We see that eq. 10-10 yields  $H_x = 0$  for  $a = R^2$  and  $r = R$ , corresponding to the case of impenetrability.)

$H_x$  is therefore proportional to  $\sin \theta$  on the boundary as well as in the external space. Remembering the intimate connection between the density and the tangential component of magnetic field, which we first noted when discussing thick specimens, it is natural to put inside the cylinder

$$I_x = I_y = 0, \quad I_z = (r / \tau) \sin \theta \quad (10-11)$$

with  $k = 0$  and  $n = 1$  must be satisfied by  $(r)$ . Furthermore  $I_z / r$  must remain finite and continuous at  $r = 0$  so that

$$f(r) = C J_1(r/\beta), \quad I_z = C J_1(r/\beta) \sin \theta \quad (10-12)$$

where  $C$  is an integration constant. From  $I_x = -c / r$ ,  $\text{curl } I$  and eq. 8-1 it follows therefore that

$$H_x = -\frac{c \lambda}{r} \frac{\partial I_x}{\partial \theta} = -\frac{c J_0 C}{r} J_1(r/\beta) \cos \theta \\ = -\frac{\sqrt{1/C}}{\beta r} J_1(r/\beta) \cos \theta \quad (10-13)$$

$r^{-1} \cos \theta$  is the real part of the function  $\zeta^{-1}$  of the complex variable  $\zeta = x + iy$  and in this way a solution of the potential equation,

and, noting one of the eqs. 8-7,

$$H_x = c \lambda \frac{\partial I_x}{\partial \theta} = -\sqrt{1/C} [I_0(r/\beta) - \frac{1}{r \beta^2} J_1(r/\beta)] \sin \theta \quad (10-14)$$

For boundary conditions we have the continuity of the two components of  $I$  at  $r = R$ . These can be satisfied by the above expressions, and this justifies our chosen procedure. As a comparison of eqs. 10-13 and 10-14 with 10-10 shows, we have only to adjust the constants  $a$  and  $C$  so that

$$H_0 \left( 1 - \frac{a}{R^2} \right) = \frac{\sqrt{1/C}}{\beta R} J_1(r/\beta) \quad (10-15)$$

$$H_0 \left( 1 + \frac{a}{R^2} \right) = \sqrt{1/C} [J_0(r/\beta R) - \frac{1}{r \beta^2} J_1(r/\beta R)] \quad (10-15)$$

These requirements yield:

$$C = \frac{2 J_0(r/\beta R)}{\sqrt{1/C} I_0(r/\beta R)}, \quad 1 - \frac{a}{R^2} = \frac{2}{\beta^2 R^2} \frac{J_1(r/\beta R)}{I_0(r/\beta R)} \quad (10-16)$$

According to eqs. 10-13 and 10-14 the magnetic lines of force in the interior of the cylinder must be such that  $I_z = \text{constant}$ . For thick cylinders this means

$$\frac{\epsilon I_z(r/\beta R)}{I_0(r/\beta R)} = -e^{-\beta(R-r)} \quad (10-17)$$

The right-hand side of the equation for  $I_z$  becomes zero, and  $a$  assumes the potential theory value  $R^2$ , and at the surface, according to eq. 10-10 we shall have

$$(H_z)_k = -2 H_0 \sin \theta \quad (10-17)$$

The maximum  $2 H_0$  of  $|H_z|$  illustrates the doubling of the field strength due to field deformation discussed in Chap. 1 (g). From eqs. 10-16 and 10-17, however, it follows that

$$I_z = -2 H_0 k^{-1/4} e^{-\beta(r-R)} \sin \theta = \lambda^{-1/4} (H_z)_k e^{-\beta(r-R)}$$

The same result would be obtained from eq. 7-10 by adapting to a cylindrical surface the equation given there for a plane boundary. Such a step would be justified for a thick cylinder. The protecting layer obeys the same laws here as at a plane surface.  $I_z$  is negative for positive  $\theta$ , i.e., in the upper part of Fig. 1-5, so the current is flowing away from the reader; this fact corresponds to the general rule that current, magnetic field, and internal normal form a right-handed system.

According to eq. 10-17 and the equation for  $a$  in 10-16 we have,

$$a = R^2 \left( 1 - \frac{2}{\beta R} \right)$$

## 10. THE CYLINDER IN A HOMOGENEOUS MAGNETIC FIELD 53

The magnetic moment is decreased by the factor  $(1 - 2\beta/R)$  compared with the case of a completely vanishing penetration depth ( $\beta \rightarrow \infty$ ). For thin cylinders ( $\beta R \ll 1$ ),  $I_1(\beta/R) = 1$  and  $I_1'(\beta/R) = \frac{1}{2}\beta/R$ . (Compare the series 8-6). The right-hand side of equation 10-16 for a now penetrates the cylinder and  $a = 0$ , according to eq. 10-9 the field now current in it, because, without being deflected and no longer induces any agreement with eq. 7-29.

According to eq. 8-6 we have the following series expansions:

$$\begin{aligned} I_1(x) &= 1 + \frac{(ix)^2}{1121} + \frac{(ix)^4}{2131} + \cdots + \frac{(ix)^{2n}}{m!(m+1)!} + \cdots \\ I_1'(x) &= 1 + \frac{(ix)^3}{1113} + \frac{(ix)^5}{(21)^3} + \cdots + \frac{(ix)^{2n+1}}{(m!)^2} + \cdots \end{aligned}$$

In the second series the coefficients of all powers of  $x$  are greater than the corresponding coefficients in the first series, therefore  $I_0'(x) > I_1(ix)/ix$ , and it increases with increasing  $x$  more rapidly than  $I_1(ix)/ix$ . The right-hand side of eq. 10-16 for  $a = 0$  is therefore smaller than unity for all values of  $\beta/R$  and continually decreases with increasing  $R$  but without becoming negative. Therefore it increases with increasing  $R$  monotonically from 0 to  $R^*$ , the limit already mentioned.

Figure 10-1 shows the form of the lines of force for three different values of  $\beta/R$ . In the external space the lines follow the same course as with a diamagnetic specimen. However, whereas inside a diamagnetic body they would be straight, here they are more or less curved. If the temperature is lowered,

starting from the transition temperature, the penetration depth  $\beta^{-1} = c/\sqrt{A}$  is at first great, and so  $\beta/R = a$  a small number for any given value of  $R$ . Later  $\beta^{-1}$  decreases and  $\beta/R$  increases, this way the gradual expulsion of the field from the interior of the specimen. The final phase,  $\beta R \gg 1$  is shown in Fig. 1-5.

As the current here has only one component  $V$ , the solution implied by eqs. 10-12, 10-15, and 10-14 can be taken over for noncubic crystals under the same conditions as set up in Chap. 8 (e).

(d) No rigorous solution can yet be given for an elliptical cylinder in an external field; just as was the case for the cylinder carrying a current treated in Chap. 8 (d), we must confine ourselves again to the approximation that holds only for "thick" cylinders. The boundary curve must then be a field line. The solution is trivial for the longitudinal field: everywhere in the external space the field strength  $H_z$  is constant and equal to  $H_0$ , and the current density can be calculated by eq. 7-10.

For the transverse field, however, we assume that the field strength forms an angle  $\theta_0 < \pi/2$  with the  $z$  axis at a great distance from the cylinder. For the complex variable  $\zeta = x + iy$ , which we shall call  $W = U + iV$ , and take  $U$  as the potential, we define  $W$  in terms of the complex parameter  $X = \psi + i\varphi$ , namely,

$$W = -\frac{1}{2}H_0\sqrt{a^2-\delta^2}\left(e^{i(-\theta_0)} + \frac{a+b}{a-b}e^{-i(-\theta_0+\varphi)}\right) \quad (10-18)$$

$$\zeta = \sqrt{\frac{X^2}{a^2-\delta^2}}\cosh\frac{X}{\delta} \quad (10-19)$$

The second of these equations follows from eq. 8-26 by putting  $a = 1$  there. In analogy to eq. 8-27 we have here

$$X = \sqrt{a^2 - \delta^2} \cosh \psi \cos \varphi, \quad Y = \sqrt{a^2 - \delta^2} \sinh \psi \sin \varphi \quad (10-20)$$

and the curves  $\psi = \text{constant}$  are the confocal ellipses:

$$\frac{X^2}{\cosh^2 \psi} + \frac{Y^2}{\sinh^2 \psi} = a^2 - b^2 \quad (10-21)$$

Let the contour of the cylinder correspond to the value  $\psi_0$ , so that

$$\frac{X^2}{\cosh^2 \psi_0} + \frac{Y^2}{\sinh^2 \psi_0} = a^2 - b^2 \quad (10-22)$$

$\psi$  and  $\varphi$  are called elliptical coordinates. To make them single valued we restrict them to the ranges of values 0 to  $+\infty$  for  $\psi$  and 0 to  $2\pi$  for  $\varphi$ . Each of the above hyperbolae thus corresponds to four  $\varphi$  values; if  $\varphi = \varphi_0$  is the semi-axis in the first quadrant ( $x > 0, y > 0$ ), then  $\varphi = \pi - \varphi_0$  is the semi-axis in the second quadrant ( $x < 0, y > 0$ ),  $\varphi = \pi + \varphi_0$  is the semi-axis in the third quadrant ( $x < 0, y < 0$ ) and  $\varphi = 2\pi - \varphi_0$  in the fourth ( $x > 0, y < 0$ ).

\*The assumption that  $\theta_0 > \pi/2$  leads to nothing new.

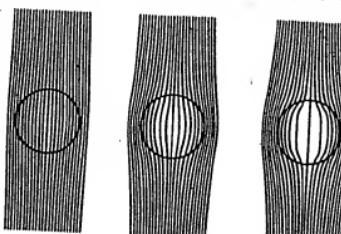


Fig. 10-1. Lines of force for a thin superconducting cylinder in a transverse homogeneous magnetic field for different ratios of diameter to penetration depth, a)  $\beta R = 1$ ; b)  $\beta R = 2$ ; c)  $\beta R = 3$

From eq. 10-18 it follows that

$$U = -\frac{1}{2} H^2 \left[ \frac{1}{a^2 - b^2} \left( e^a + \frac{a+b}{a-b} e^{-a} \right) \cos(\varphi - \theta_0) \right]$$

$$V = -\frac{1}{2} H^2 \left[ \frac{1}{a^2 - b^2} \left( e^a - \frac{a+b}{a-b} e^{-a} \right) \sin(\varphi - \theta_0) \right] \quad (10-23)$$

Because of the way they were derived from eq. 10-18,  $U$  and  $V$  are solutions of the potential equation.  $\psi$  is infinite at infinity, according to eq. 10-19. Therefore at infinity

$$U = -\frac{1}{2} H^2 \left[ \frac{a+b}{a-b} e^a (\cos \varphi \cos \theta_0 + \sin \varphi \sin \theta_0) \right]$$

The field is therefore homogeneous at infinity, and inclined at an angle  $\theta_0$  to the  $x$  axis. The field line  $V = 0$  consists first of those parts of the hyperbolas  $\varphi = \theta_0$  and  $\varphi = \pi\pi + \theta_0$ , which lie outside the ellipse  $\psi_0$ , since these formulas are valid outside, and secondly of the ellipse  $\psi_0$ . Because according to eq. 10-21 on this ellipse

$$e^{2\varphi} = \frac{a+b}{a-b} e^{-2\varphi}$$

The expression 10-18 thus satisfies all the imposed conditions. We proceed to the calculation of  $|H| = |\partial W/\partial z|$ . From eq. 10-18

$$\begin{aligned} \frac{dW}{dz} &= \frac{(dW/dz)}{(dz/dz)} = -2 \sinh \left[ \frac{(a^2 - b^2)}{a - b} \cdot \frac{a + b}{a - b} \cdot z + \varphi \right] \\ H^0 &= \frac{H^0 (a + b, \varphi - \theta_0, -c^2 \psi + (r\varphi - \theta_0))}{\frac{1}{a - b} \left( \frac{a + b}{a - b} \cdot e^{-2\varphi} - c^2 \psi - (r\varphi - \theta_0) \right)} \end{aligned}$$

Along the ellipse  $\psi_0$  we have from eq. 10-21

$$|H| = \left| \frac{dW}{dz} \right| = \frac{H^0 (a + b) \sin(\varphi - \theta_0)}{\sqrt{a^2 \sin^2 \varphi + b^2 \cos^2 \varphi}}$$

The maximum of this expression is at the point where

$$\tan \varphi = -\frac{b^2}{a^2} \cot \theta_0, \quad i.e., \frac{y}{x} = -\frac{b^2}{a^2} \cot \theta_0$$

a diameter of the ellipse is drawn in the direction  $\theta_0$ , the conjugate diameter (parallel to the tangents at the ends of the first one) is given by

$$\frac{y}{x} = -\frac{b^2}{a^2} \cot \theta_0$$

If  $b \ll a$ , the maximum field therefore lies considerably nearer to the major axis of the ellipse than this diameter, except when  $\theta_0 = 0$  or  $\frac{1}{2}\pi$ . The maximum value itself amounts to

$$|H|_{max} = H^0 \left( \frac{1}{a} + \frac{1}{b} \right) \sqrt{a^2 \sin^2 \theta_0 + b^2 \cos^2 \theta_0} \quad (10-24)$$

## 11. THE SPHERE IN A HOMOGENEOUS MAGNETIC FIELD

For  $\theta_0 = 0$  the factor multiplying  $H^0$  becomes  $(1 + b/a)$  and is thus smaller than the factor 2 appearing in the circular cylinder. For  $\theta_0 = \frac{1}{2}\pi$  however, the factor becomes  $1 + b/a > 2$ . This confirms the statement made in Chap. 1(e) about the intensification of the field. It is at once evident that this intensification is greater when the cylinder forces the field to diverge around its major axis than if it exposed only its minor axis to the field.

The expression 10-24 is needed to calculate the limiting value of  $H^0$  that destroys the superconductivity in the cylinder [Chap. 17 (f)].

### CHAPTER 11

#### The Sphere in a Homogeneous Magnetic Field

(a) We introduce polar coordinates in space,  $r, \theta, \varphi$ , forming a right-handed system in that order (Fig. 11-1). The following equations hold for the curl of a vector  $A$

$$\text{curl } A = \frac{1}{r \sin \theta} \left[ \frac{\partial}{\partial \theta} (\sin \theta A_\varphi) - \frac{\partial A_\theta}{\partial \varphi} \right] \quad (11-1)$$

$$\text{curl}_\theta A = \frac{1}{r \sin \theta} \frac{\partial A_r}{\partial \varphi} - \frac{1}{r} \frac{\partial (A_\theta)}{\partial r} \quad (11-2)$$

$$\text{curl}_\varphi A = \frac{1}{r} \frac{\partial (r A_\theta)}{\partial r} - \frac{1}{r^2} \frac{\partial A_r}{\partial \varphi} \quad (11-3)$$

The differential equation  $\mathcal{L} + \beta^2 u = 0$  in these coordinates reads:

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial u}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 u}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta \cos^2 \varphi} \frac{\partial^2 u}{\partial \varphi^2} - \beta^2 u = 0 \quad (11-2)$$

We can solve this equation for the present problem by separation of the variables:

$$u = (r) \sin \theta \cos \varphi \quad (11-5)$$

Direct calculation shows that

$$\frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta \cos^2 \varphi} \frac{\partial^2 u}{\partial \varphi^2} = -\frac{2}{r^2} / (r) \sin \theta \cos \varphi$$

so we can divide eq. 11-2 by the factor  $\sin \theta \cos \varphi$  common to all terms and we are left with the ordinary differential equation for  $(r)$ :

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{du}{dr} \right) - \left( \beta^2 + \frac{2}{r^2} \right) u = 0 \quad (11-4)$$

The solution of this that remains finite at  $r = 0$  is

$$\begin{aligned} /(\nu) &= \frac{1}{\beta r} \cosh(\beta r) - \left(\frac{1}{\beta r}\right)^3 \sinh(\beta r) \\ &= \frac{(\beta r)^2}{3} + \frac{(\beta r)^4}{5 \cdot 3!} + \cdots + \frac{(\beta r)^m}{(m+2) \cdot m!} + \cdots \end{aligned} \quad (11-5)$$

/ is positive because  $\tanh \beta r \leq \beta r$  for all positive values of  $\beta r$ . For large values of  $\beta r$

$$/ = \frac{1}{2} (\beta r)^{-1} e^{\beta r} \quad (11-6)$$

(b) Let the polar axis  $\theta = 0$  and likewise the positive  $x$  axis be in the direction of the homogeneous magnetic field. If the field were undisturbed its potential would be

$$\Phi_0 = -H^0 r \cos \theta$$

If the sphere were completely impermeable to the lines of force it would act as a dipole, as shown by potential theory and as will be confirmed later. Therefore to the potential  $\Phi_0$  a term of the form  $r^{-1} \cos \theta$  follows immediately from eq. 11-7:

$$\Phi = -H^0 \left(r + \frac{a}{r}\right) \cos \theta \quad (11-7)$$

Here  $4\pi a H^0$  represents the magnetic moment of the sphere\*. With positive  $a$  it is in the negative  $x$  direction and thus opposite to the field. The magnetic field strength  $H = -\nabla \Phi$  follows immediately from eq. 11-7:

$$H_x = -\frac{\partial \Phi}{\partial r} = H^0 \left(1 + \frac{2a}{r^2}\right) \cos \theta \quad (11-8)$$

$$H_y = -\frac{1}{r} \frac{\partial \Phi}{\partial \theta} = -H^0 \left(1 + \frac{a}{r^2}\right) \sin \theta \quad (11-8)$$

As can be expected from symmetry the lines of force lie in meridian planes  $\varphi = \text{constant}$ . According to Chap. 7 (e) the current must be perpendicular to the lines of force, at least for thick superconductors, and

\* Together with  $r^{-1}$  itself, all its derivatives with respect to the rectangular coordinates  $x, y, z$  are also solutions of  $\Delta u = 0$ . But  $\partial(r^{-1})/\partial x = -x/r^2 = -\cos \theta$ .

\*\* This is in Lorentz units. In electrostatic units the moment is  $a H^0$ .

near the surface, so we must expect it to flow along the latitude — circles  $r = \text{const.}, \theta = \text{constant}$ . Therefore for the interior of the sphere we try

$$l_\theta = i_\theta = 0, \quad l_r = C/(r \sin \theta) \quad (11-9)$$

If for  $|r|$  we assume the same function as in eq. 11-5, then according to (a) the components of the current

$$l_\theta = -l_\rho \sin \varphi, \quad l_r = l_\rho \cos \varphi \quad (11-10)$$

satisfy the differential equation  $\Delta u - \beta^2 u = 0$ . From the relation  $H_{\text{ext}} - \epsilon A$  curl  $A$  we have from eq. 11-1:

$$H_r = -\frac{c \lambda}{r \sin \theta} \frac{\partial \sin \theta l_\rho}{\partial \theta} = -\frac{2\sqrt{\lambda}}{\beta r} C/(r \cos \theta) \quad (11-10)$$

$$H_\theta = \frac{c \lambda}{r} \frac{\partial l_\rho}{\partial \theta} = \frac{1}{\beta C} [\sinh(\beta r) - \gamma] \sin \theta$$

To check whether these equations are correct we show, as in Chap. 10 (e), that they fulfill the boundary conditions at the surface of the sphere  $r = R$ . These require the continuity of the two nonvanishing components of  $H$ . According to eqs. 11-8 and 11-10 we should have

$$H^0 \left(1 - \frac{2a}{R^2}\right) = \frac{2\sqrt{\lambda}}{\beta R} C/(R)$$

$$H^0 \left(1 + \frac{a}{R^2}\right) = \frac{\sqrt{\lambda} C}{\beta R} U(R) - \sinh(\beta R) \quad (11-11)$$

As a matter of fact we can satisfy these conditions by means of the adjustable constants  $a$  and  $C$ . For this purpose we have to put

$$C = -\frac{3 H^0 \beta R}{2 \sqrt{\lambda} \sinh(\beta R)}, \quad a = \frac{1}{2} \left[1 - \frac{3 U(R)}{\sinh(\beta R)}\right] R^2 \quad (11-11)$$

Evidently  $l_\theta$  is negative; the current flows against the arrow in Fig. 11-1.

From eq. 11-10 we now have the equations

$$\frac{\partial}{\partial r} (r \sin \theta l_\rho) dr + \frac{\partial}{\partial \theta} (r \sin \theta l_\rho) d\theta = 0, \quad \text{i.e., } r \sin \theta l_\rho = \text{constant}$$

$$\text{or } r/(r) \sin^3 \theta = \text{constant}. \quad \text{These, with } \varphi = \text{constant}, \text{ determine the magnetic lines of force in the interior.}$$

(c) The discussion proceeds in the same way as in Chap. 10 (e). From eqs. 11-9, 11-10, and 11-11 it follows that for a large sphere ( $\beta R \gg 1$ ) and high values of  $\beta r$  that

$$l_\theta = -\frac{3 H^0 R}{2 \sqrt{\lambda} r} e^{-\beta(r-1)} \quad (11-12)$$

$$H_x = 0, \quad H_y = -\frac{3 H^0 R}{2 r} e^{-\beta(r-1)} \sin \theta$$

Again this means the formation of a protective layer around a field-free interior. Furthermore, we conclude from eqs. 11-11 and 11-6 that

$$\alpha = \frac{1}{2} \left( 1 - \frac{3}{\beta R} \right) R^3 \quad (11-15)$$

Using this value it follows from eq. 11-8 in agreement with eq. 11-12 that at  $r = R$ :

$$H_r = 0, \quad H_\theta = -\frac{3}{2} H_0 \sin \theta \quad (11-14)$$

The first equation proves that in this approximation the sphere appears from the outside as if it were totally impenetrable to the lines of force; the second equation proves that the intensification of the field due to distortion leads to a maximum one and a half times the original field strength  $H_0$ , as already mentioned in Chap. 1 (6). Figure 1-5 is valid qualitatively for the field distribution in a meridian plane of the sphere in spite of the fact that it is drawn for the cylindrical problem. For small  $\beta R$  becomes (1/3)  $\beta R$  from eq. 11-11 we have

$$\alpha = 0 \quad (11-15)$$

As at the same time  $C = -\frac{3}{2} H_0$ , it follows from eq. 11-9 that

$$i_r = -\frac{1}{2} H_0 \left( \frac{\beta r}{R} \right) \sin \theta \quad (11-16)$$

and from eq. 11-10 that

$$H_r = H_0 \cos \theta, \quad H_\theta = -H_0 \sin \theta \quad (11-17)$$

According to the last equation  $H$  is in the  $x$  direction and has the magnitude  $H_0$ . The magnetic field penetrates the sphere without hindrance as to be expected from Chap. 7 (f), whereas eq. 11-16 for  $\mathbf{i}_r$  has the same general form as eq. 7-29. Choosing the length of the superconductor  $L$  equal to  $R$  in order to duplicate eq. 11-16 one has to put  $-\frac{3}{2} (r/R) \sin \theta$  for the pure number  $\gamma_0$  which depends only on the position of the origin in the superconductor.

We conclude from the expansion 11-5 and the known series

$$\sinh(\beta R) = \beta R + \frac{(\beta R)^3}{3!} + \frac{(\beta R)^5}{5!} + \cdots + \frac{(\beta R)^{2m+1}}{(2m+1)!} \cdots$$

that  $\sinh(\beta R)$  increases faster with increasing  $\beta R$  than  $(\beta R)$ . Therefore by eq. 11-11  $\alpha$  grows monotonically with  $\beta R$  from 0 to  $\frac{3}{2} R^2$ , the magnetic

<sup>1</sup> It follows from eq. 11-10 for the center of the sphere  $r = 0$  exactly

$$(H_r)_{r=0} = \frac{H_0 \beta R \cos \theta}{\sinh(\beta R)}, \quad (H_\theta)_{r=0} = -\frac{H_0 \beta R \sin \theta}{\sinh(\beta R)}.$$

This gives  $\mathbf{H}$  the direction of the  $x$  axis, as was to be expected from symmetry, and the magnitude  $H_0 \beta R \tanh(\beta R)$ . This can be used to confirm the mean value theorem of eq. 7-25.

## 11. THE SPHERE IN A HOMOGENEOUS MAGNETIC FIELD

moment  $4\pi a H_0$  goes from 0 to  $2\pi R^2 H_0$  and the moment per unit volume and unit field strength increases from 0 to  $\frac{3}{2} \frac{R^2}{R}$ .

A nonmagnetic layer, e. g., of colloidal spheres of mercury dispersed in gelatine, must become increasingly diamagnetic below the transition temperature,  $4.17^\circ K$ , the greater the moment per unit volume due to the spheres.

If there are  $N$  such spheres per unit volume, the latter has a moment  $4\pi a N H_0$ ; the permeability is therefore  $\chi' = 4\pi a N$ . If each sphere has a radius  $R$  and they occupy a fraction  $V$  per unit volume, then  $N = 3 V / 4\pi R^3$  so that

$$\chi' = \frac{3 V a}{R^3}$$

For large values of  $\beta R$ :

$$a = \frac{1}{2} R^3 \quad \text{according to Fig. 11-2. Relative susceptibility of a slab containing superconducting colloidal mercury spheres as a function of temperature. (After Shoenberg.)}$$

corresponding permeability

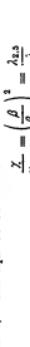
$$\chi'' = \frac{3 V'}{R^3}$$

and in this way we get for  $\beta R \ll 1$  a somewhat better approximation than used above:

$$\chi'' = \frac{a}{\frac{3}{2} \frac{R^2}{R}} = 1 - \frac{3/(R)}{\sinh(\beta R)} = \frac{1}{15} (\beta R)^4 \quad (11-18)$$

(d) Shoenberg<sup>4</sup> (Chap. 1 (c)) used the above method to determine the superconductivity constant  $\lambda_0$  as a function of temperature. He knew from the amount of mercury in emulsion what the permeability  $\chi_0$  would be if the  $\beta R$  of the small spheres were great compared with unity. Actually the permeability was only some thousands of this (see Fig. 11-2) and dropped much lower still as the transition temperature was approached. Shoenberg knew only that the average radius of the spheres was about  $0.5 \times 10^{-4}$  cm. To obtain information about  $\beta$  he started from eq. 11-18. If we indicate values of  $\chi_0$ ,  $\beta$ , and  $T = 2.5^\circ K$  by an inferior 2, we have, from eqs. 11-18 and 7-

<sup>4</sup>D. Shoenberg, *Nature*, 148, 434 (1939). E. Laermann and D. Shoenberg, *Nature*, 160, 747 (1948).



By means of this equation Shoenberg was able to plot his experimental data as in Fig. 11-3, which shows  $\sqrt{J}/\sqrt{\rho}$  as a function of  $T_c$ . They agree excellently with the values found by Applédard and co-workers<sup>47</sup> (Chap. 18 [e]).

(g) If we specify a line of force with its distance in the undistorted part of the sphere, its equation can easily be derived from eq. 11-7 and reads

$$\left(r^2 - \frac{2a}{r}\right) \sin \theta = C^*, \quad \varphi = \text{constant}$$

The value  $C/R$  of those lines of force that just touch the sphere at its equator is an approximate measure of the field distortion. The results are shown in Table 11-1. The third column shows the decrease of the magnetic moment. All lines of force with smaller  $C/R$  pass through the sphere; all lines of force with larger  $C/R$  avoid it completely.

Table 11-1

$\mu R$	$C/R$	$a/R^2$
80	0	0.50
20	0.38	0.43
10	0.65	0.41
6	0.69	0.29
5	0.75	0.22
4	0.82	0.17
3	0.90	0.091
2	0.92	0.077
1		

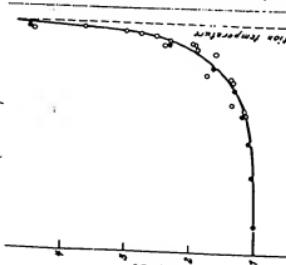


Fig. 11-3. The superconductivity constant,  $\sqrt{J}/\sqrt{\rho}$ , as a function of temperature,  $T_c$  for mercury as a function of temperature,  $T$  for mercury as a function of temperature,  $T$  measurements of Applédard, Bästow, and London.<sup>47</sup> Measurements of Shoenberg.

(f) The eqs. 11-9, 11-10, and 11-11 remain true for noncubic crystals if the ellipsoid of the tensor  $\lambda_{ij}$  has rotational symmetry and the axis of symmetry lies in the  $x$  direction. Only then  $\beta_1$  can be replaced by  $\beta_1 = 1/c/\sqrt{A_1}$  where  $A_1$  is the principal value of the tensor for a direction perpendicular to the axis of symmetry.

<sup>47</sup> T. S. Applédard, T. R. Branson, and H. London, *Nature*, 148, 453 (1939).

## CHAPTER 12

## Persistent Currents

(a) A classical method for the treatment of electromagnetic problems uses the vector potential  $A$  in conjunction with the scalar potential  $\Phi$ . In the static case  $A$  becomes the electrostatic potential and it is therefore a generalization of the latter.  $A$  and  $\Phi$  are defined by requiring

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (12-1)$$

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \nabla \Phi \quad (12-2)$$

From these it follows at once that

$$\operatorname{div} \mathbf{B} = 0, \quad \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = -\operatorname{curl} \mathbf{E} \quad (12-3)$$

which agrees with the fundamental eqs. I and III (Chap. 3). To obtain the fundamental eqs. II and IV also we must now add a condition on  $\operatorname{div} \lambda$ , which we may do because no vector is completely defined by giving only its curl. We require that

$$\operatorname{div} \mathbf{A} + \frac{\epsilon \mu}{c^2} \frac{\partial \Phi}{\partial t} = 0 \quad (12-4)$$

According to eqs. 12-2 and 3-1 we now have

$$\operatorname{div} \mathbf{D} = \operatorname{div} (\epsilon \mathbf{E}) = \epsilon \operatorname{div} \mathbf{B} + (\mathbf{E} \cdot \operatorname{grad} \epsilon) \quad (12-5)$$

$$= -\frac{\epsilon}{c} \frac{\partial}{\partial t} \operatorname{div} \mathbf{A} - \epsilon \mathcal{D} \Phi + (\mathbf{E} \cdot \operatorname{grad} \epsilon)$$

and if we subject  $\Phi$  to the condition

$$\frac{\partial \Phi}{\partial t} - \frac{\epsilon \mu}{c^2} \frac{\partial \Phi}{\partial t^2} = -\rho + \frac{1}{c} (\mathbf{E} \cdot \operatorname{grad} \epsilon) \quad (12-6)$$

we recover eq. IV ( $\operatorname{div} \mathbf{D} = \rho$ ). In order to obtain eq. II we use eqs. 12-1, and 12-3 and the vector rule 6-1 to obtain

$$\operatorname{curl} \mathbf{B} = \operatorname{curl} \operatorname{curl} \mathbf{A} = \operatorname{grad} \operatorname{div} \mathbf{A} - \mathcal{D} \mathbf{A} = -\operatorname{grad} \left( \frac{\epsilon \mu}{c^2} \frac{\partial \Phi}{\partial t} \right) - \mathcal{D} \mathbf{A} \quad (12-7)$$

$$= \frac{\epsilon \mu}{c^2} \left[ \frac{\partial \Phi}{\partial t} + \frac{1}{c} \frac{\partial^2 \Phi}{\partial t^2} \right] - \frac{1}{c} \frac{\partial \Phi}{\partial t} \operatorname{grad} (\epsilon \mu) - \mathcal{D} \mathbf{A} \quad (12-8)$$

Also according to eqs. 3-2 and II:

$$\operatorname{curl} \mathbf{B} = \operatorname{curl} (\mu \mathbf{H}) + \operatorname{curl} (\mu \operatorname{curl} \mathbf{H}) - [\mathbf{H} \times \operatorname{grad} \mu] \perp \operatorname{curl} \mathbf{H} \quad (12-9)$$

$$= \frac{\mu}{c} \left( \frac{\partial \mathbf{E}}{\partial t} + \mathbf{H} \right) - [\mathbf{H} \times \operatorname{grad} \mu] + \operatorname{curl} \mathbf{M} \quad (12-10)$$

The necessary and sufficient condition for the validity of eq. 11 follows by subtracting the right-hand sides of 12-5a and 12-5b:

$$dA - \frac{e\mu}{c^2} \frac{\partial A}{\partial t} = -\frac{\mu_1}{c} - \text{curl } M + \frac{1}{c} \frac{\partial \Phi}{\partial t} + [H \times \text{grad } \mu] \quad (12-6)$$

We accept eqs. 12-4 and 12-6 as valid throughout all space. The 1 here always means the sum of ohmic and supercurrents.

The most frequent application of eq. 12-1 consists in the transformation of the integral  $\int B \cdot d\sigma$  over a surface  $C$  into the line integral around the boundary by Stokes' theorem:

$$\int_C (B \cdot d\sigma) = \int_C (A \cdot d\sigma) \quad (12-7)$$

Figure 12-1 shows the relation between the direction of the normal vector  $d\sigma$  and the sense  $d\sigma$  in which the line integral traverses the boundary. The justification for using the same symbol  $C$  to both surface and loop is that all surfaces with the same loop as boundary have the same eq. 12-7. The integral  $\int_C (B \cdot d\sigma)$  because of  $\text{div } B = 0$ .

(b) We now have to explain the concept of the multiply connected region. In a simply connected or singly connected region of space two closed curves  $C$  and  $C'$  which lie completely within the region, but are otherwise quite arbitrary, can be transformed into each other by continuous deformation without either of them leaving the region. In particular  $C$  can be contracted to a point, because  $C'$  can be chosen to be an infinitesimal loop around this point. Such curves also exist in a doubly connected region; we call them curves of the first kind. Besides these there are curves of the second kind which can be transformed in the described manner into each other but not into curves of the first kind. It is impossible to reduce them to a point (Fig. 12-2a).

We have to distinguish 2 sets of curves for an  $n$ -ply connected region<sup>1</sup>. All curves of the same kind can be transformed into each other in the described manner but not curves of one set into curves of another set. The possibility of reduction to a point is reserved for curves of the first kind. We assign one and for all the same arbitrary sense of traversal to all curves of the same kind. The line integrals over such curves are defined to follow this sense of traversal, which we shall call the sense of the curve or circuit.

<sup>1</sup>Curves that can be reduced by continuous deformation to a curve  $C_1$  together with a curve  $C_2$  within a triply connected region do not constitute a new kind of curve. A similar statement holds for  $n$ -ply connected regions.

In a singly connected region of space every finite and continuous scalar function  $\Psi$  is unique if its gradient is uniquely defined, e. g., by physical quantities, because for any closed curve  $C$  in the region

$$\int_C (ds \cdot \text{grad } \Psi) = \int_C (ds \cdot \text{curl grad } \Psi)$$



FIG. 12-2. (a) Curves  $C_1$  and  $C_2$  in a doubly connected region. (b) Curves  $C_4$  and  $C_5$  in a triply connected region. The dotted line is not a new kind of curve because it can be reduced to a curve  $C_5$  together with a curve  $C_4$ .

and the right side vanishes because  $\text{curl grad } \Psi \equiv 0$ . This conclusion holds only for curves of the first kind in a doubly connected region if  $\Psi$  is defined only within the region. Since these curves can be contracted to a point, we can draw surfaces of which they are the boundaries completely within the region of interest. For a curve of the second kind, such a surface necessarily extends outside the region. Otherwise it would also be possible to reduce these curves to a point. Consequently, for a curve of the second kind  $C_5$ ,

$$\int_{C_5} (ds \cdot \text{grad } \Psi) = S_C,$$

the surface integral extends over a surface bounded by the curves  $C_4$  and  $C_5$  lying completely within the region and is therefore zero because of the present theorem. In an  $n$ -ply connected region the integral

$$\int_{C_1} (ds \cdot \text{grad } \Psi) - \int_{C_2} (ds \cdot \text{grad } \Psi) = \int_{C_3} (ds \cdot \text{curl grad } \Psi)$$

can differ from zero and be either positive or negative. However, the integral has the same value for all curves  $C_1$ . For two such curves  $C_4$  and  $C_5$ , the integral

$\int_{C_4} (ds \cdot \text{grad } \Psi) - \int_{C_5} (ds \cdot \text{grad } \Psi)$

but has different values for curves of different kind. It is zero for curves of the first kind, as before.

A doubly connected region is made simply connected by a cut  $Q$ , i.e.,

a surface intersecting every curve  $C_4$  once and only once, destroying all  $C_4$  closed curves. All curves still remaining closed are now of the first kind.

The boundaries of the cut necessarily lie in the surface of the region.

Otherwise  $Q$  would not cut all the curves  $C_n$ . Except for this requirement there is complete freedom of choice of position and form of  $Q$ .  $Q_n$  ( $n = 2, 3, \dots, n$ ) are needed to produce a simply connected region from an "only" connected one.  $Q_n$  cuts all closed curves  $C_n$ . In the single region formed in this way only closed curves of the first kind can exist and the scalar  $\Psi$  is unique in such a region. Consider two points 1 and 2 lying on opposite sides of, and immediately adjacent to, the cut  $Q_n$ .  $\Psi$  differs at 1 and 2 by

$$\Psi_2 - \Psi_1 = \int_{C_n} (ds \cdot \nabla \Psi) = \int_{C_n} (\psi S \cdot ds)$$

The points 1 and 2 must be chosen in such a way that the path from 1 to 2 that does not pass through the cut  $Q_n$  has the same sense as the curve  $C_n$ . As  $S_{C_n}$  has the same value for all curves  $C_n$ , the jump in  $\Psi$  at the cut is  $\delta$  for all points on it.

These cuts are necessary if one wishes to apply Stokes' theorem in a multiply connected region to vector  $\Psi S$ , the product of a unique vector  $S$  with  $\Psi$ . Applied to the cut region

$$\int \operatorname{div}(\Psi S) ds = - \int \Psi S \cdot ds$$

and every cut  $Q_n$  makes two contributions to the surface integral which differ formally only in the directions of the inner normals  $ds_1$  and  $ds_2$ . The sum of these two contributions is

$$-(\Psi_1 - \Psi_2) \int_{C_n} (S \cdot ds) = S_{C_n} \int (S \cdot ds) \quad (12-8)$$

The fact that the two contributions do not in general cancel each other proves that the Gauss theorem can be applied directly only to singly connected regions. According to what has been agreed to about the points 1 and 2, the normal  $ds_1$  has the same direction as the sense of the curves  $C_n$ .

(c) From eq. 12-1 and the fundamental equation  $X \cdot H = -c \operatorname{curl} G$  it follows that

$$\operatorname{curl}(cG + A) = 0 \quad (12-9)$$

before a superconductor scalar potential  $\Psi$  exists for which

$$\operatorname{grad}\Psi = cG + A \quad (12-10)$$

As there is no superconductor outside the superconductor this potential is defined only in the interior. The integral

$$S_C = \int_C (ds \cdot \nabla \Psi) = \int_C ds(cG + A) \\ = c \int_C (i \cdot ds + B \cdot dr) \quad (12-11)$$

therefore has the value zero for any closed curve  $C$  in a singly connected superconductor; in a doubly connected superconductor (in the form of a ring) it is likewise zero for curves of the first kind, but has in general a unique value  $S_{C_n}$  different from zero. In an  $n$ -ply connected superconductor the integral has the same value  $S_{C_n}$  for all curves of the  $n$ th kind. The superconducting potential  $\Psi$  is multiple valued ("periodic") with the periods " $S_{C_n}$ ".

We differentiate eq. 12-10 with respect to time and use the fundamental equation  $iX = (R = \partial G / \partial t)$  and also eq. 12-2 to obtain

$$-c \operatorname{grad}\Phi = \operatorname{grad} \frac{\partial \Psi}{\partial t} \quad (12-12)$$

The potential  $\Phi$  is defined in all space, and is therefore unique. Integrating eq. 12-12 over a closed curve  $C_n$  within the superconductor:

$$\int_{C_n} (ds \cdot \nabla \Phi) = \frac{dS_{C_n}}{dt} = 0 \quad (12-13)$$

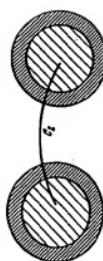
The integrals  $S_{C_n}$  do not change with time so long as the specimen remains superconducting. This is still true if during a phase transition the superconducting material grows at the expense of the normal material, so causing the ring to become thicker or, if it shrinks, by the reverse process.

The explanation of the persistent current contained in these theories is due to F. London. All experiments on the persistent current have been done with doubly connected superconductors, e. g., in the form of a ring or a closed coil. Moreover, the superconductor has always been thick compared with the penetration depth. If the curve  $C_n$  is placed in the field-free interior,  $\Phi = 0$  on the curve and it follows from eq. 12-11 that

$$S_C = \int_C B \cdot dr \quad (12-14)$$

From this eq. 12-13 shows that the flux of induction through any surface that encloses the bore of the ring and protrudes through the protective layer into the field free interior (which adds but little) is constant, see Fig. 12-3.

Therefore if a ring has been placed in a magnetic field while still above its transition temperature, and if on cooling below the transition a certain flux of induction is trapped in the bore of the ring, this will remain there until superconductivity is destroyed: it is "frozen in." If the external field



is switched off, the ring acts as a permanent magnet due to this flux of induction. The great achievement of the London theory is that it logically combines this freezing in process with the Meissner effect, i. e., the fact that the field inside a superconductor does not get frozen in but is expelled if a superconducting ring initially free of current is placed in a magnetic field, the lines of force will go around it according to Eq. 12-14; its bore remains permanently field free.

It should be emphasized once more that Eq. 12-14 holds only for "thin" rings; for "thin" ones the line integral in  $S_C$  (Eq. 12-11) cannot be neglected. In such rings the flux of induction does not freeze in. Immediately below the transition temperature every specimen has effectively thin, as has been repeatedly pointed out. The flux which according to Eq. 12-14 remains constant, is not necessarily identical with the flux that passed through the bore before the ring became superconducting.

The ohmic current has not been mentioned in the above discussion, but we have neglected it. On the contrary our conclusions are completely rigorous and independent of what happens to the ohmic current during the changes under consideration. Strictly speaking, the ohmic current has always to play its role as consumer of energy during the processes, the more strongly the more rapid the process. The fact that nothing of this kind can be detected in actual experiments, is due to the relatively slow rate of change at practicable frequencies.<sup>1</sup>

<sup>1</sup>In multiply connected specimens carrying a persistent current the superconducting potential is certainly not zero everywhere, according to the argument in the text.

However, we may ask whether perhaps it does not vanish identically for a connected superconductor in static magnetic field? This question has to be answered in the negative, in so far as we understand by A the potential introduced in (e) and describing the total magnetic field. This can already be seen for the cubic crystal where especially simple conditions prevail because  $\mathbf{A}$  and  $\mathbf{Q}$  have the same directions. Owing to Eq. 12-10 and the boundary condition  $\mathbf{A}_r = \mathbf{0}$  (and therefore also  $\mathbf{Q}_r = \mathbf{0}$ ) we must have

$$\frac{\partial V}{\partial n} = \mathbf{A}_n,$$

and it is certainly not generally true that  $\mathbf{A}_n = \mathbf{0}$ . However, by relinquishing the representation of the whole field, we could introduce a potential for the interior of the superconductor alone:

$$\mathbf{A}' = \mathbf{A} - \text{grad } \Psi$$

For this potential we should have

$$\epsilon(\mathbf{A}' + \mathbf{A}') = 0$$

Equation 12-1 would be retained in the form  $\mathbf{H} = \text{curl } \mathbf{A}'$ . Whereas according to Eq. 12-3  $\text{div } \mathbf{A} = 0$  for stationary fields generally, the relation  $\text{div } \mathbf{A}' = 0$  would follow from Eq. 12-10 only for cubic crystals. It is only for these crystals that the equation  $\text{div } \mathbf{A}' = 0$  follows from  $\text{div } \mathbf{V} = 0$ . Because of this restriction, no special significance can be attached to the potential  $\mathbf{A}'$ .

(d) Let us calculate the "period" of the superconducting potential

$$S_C = \int \mathbf{H} \cdot d\mathbf{s} = 2\pi \int_0^{\infty} r H_r dr$$

in the example of a hollow cylinder of cubic material, with an inner radius  $R$  and field  $H_i$  in the interior hollow space [Chap. 9(e)]. The integral with respect to  $r$  should extend as far as a circle situated in the protected field-free space inside the superconductor. This is expressed in the formula by writing the upper limit as infinite. Now for  $r < R$ ,  $H_r = H_i$ , whereas for  $r > R$ , according to Eq. 10-7

$$H_r = H_i \frac{H_0(i/\beta R)}{H_0(i/\beta R)}$$

so according to the theorem

$$\int_{\zeta}^{\infty} \zeta H_0(\zeta) d\zeta = -x H_1(x)$$

we obtain

$$S_C = 2\pi R^3 H_i \left[ \frac{1}{2} - \frac{1}{\beta R} H_1(i/\beta R) \right]$$

The second term in the bracket is positive real, as it should be, because both  $\cdot H_1(i/\beta R)$  and  $-H_1(i/\beta R)$  are also positive real. For large  $\beta R$  this term is vanishingly small compared with the first term because the ratio of the two Hankel functions becomes unity. For small  $\beta R$ , however, it becomes the dominant term, even increasing without limit as  $\beta R$  decreases, because  $-H_1(i/\beta R)$  becomes  $2/\pi \beta R$ , and  $H_0(i/\beta R) \rightarrow -(2/\pi) \ln(\beta R)$  in this limit. Thus we get

$$S_C = -\frac{1}{\beta^3 \ln(\beta R)} 2\pi R H_i \quad (12-15)$$

$S_C$  therefore vanishes when  $R = 0$  as in this case, of course, the hollow cylinder becomes a simply connected solid cylinder. If we imagine the temperature of a given hollow cylinder to be increased, then its  $\lambda$  increases, and consequently  $\beta$  and  $\beta R$  decrease, approaching zero when the transition temperature  $T_c$  is reached. The factor multiplying  $H_i$  increases without limit, and since  $S_C$  remains constant, according to what has been said above,  $H_i$  must accordingly decrease. The physical reason for this is the increase in the penetration depth  $\beta^{-1}$ . The field penetrates the superconductor and spreads over a continuously increasing area, so its intensity has to decrease because of the constancy of the total flux  $S_C$ . The superconducting potential  $\Psi$  is proportional to the angle  $\theta$  because of axial symmetry: thus

$$\Psi = \frac{\theta}{2\pi} S_C$$

## 12. PERSISTENT CURRENTS

and  $\Psi$  satisfies the potential equation  $\nabla^2 \Psi = 0$ . This must be so for all stationary currents in cubic-crystal superconductors according to eqs. 12-10 (e). When there is a persistent current in ring, it has a magnetic moment. Does the direction of the moment depend on the way in which it has been produced? This and similar questions are answered by the uniqueness theorem for a superconductor in a stationary field. We derive it now under the assumption that no ohmic current is supplied from outside.

We form the scalar product of 12-10 with  $\mathbf{H}/c$ , and integrate over the volume or an arbitrary (homogeneous or inhomogeneous) superconductor as indicated by the suffix  $s$  under the integral sign. This yields

$$\frac{1}{2} \int (\mathbf{H} \cdot \mathbf{H}) d\tau + \frac{1}{2c} \int (\mathbf{A} \cdot \mathbf{H}) d\tau = \frac{1}{2c} \int (\mathbf{H} \cdot \nabla \Psi) d\tau \quad (12-16)$$

Using the formula

$$(\mathbf{H} \cdot \nabla \Psi) + \Psi \nabla \cdot \mathbf{H} = \nabla \cdot (\Psi \mathbf{H})$$

the right-hand integral in eq. 12-16 can be transformed into

$$-\frac{1}{2c} \int (\Psi \nabla \cdot \mathbf{H}) d\tau - \frac{1}{2c} \int (\Psi \cdot \nabla \mathbf{H}) d\tau$$

Now because of the assumed stationary conditions in the interior, the fundamental eq. VII becomes  $\operatorname{div} \mathbf{H} = 0$ , and at the surface eq. 3-7 gives  $\mathbf{H} = 0$ . Therefore nothing remains of the above expressions except the contribution of the cross-sectional cuts which eventually have to be introduced. For the time being we assume the superconductor to be doubly connected so we need only one cut. By eq. 12-8 its contribution is

$$-\frac{1}{2c} \int (\Psi_1 - \Psi_2) \int (\mathbf{H} \cdot \nabla \Psi) d\tau = \frac{1}{2c} \int S_c \int \mathbf{H} \cdot d\sigma_1 \quad (12-17)$$

We write

$$\int \mathbf{H} \cdot d\sigma_1 = I_1 \quad (12-18)$$

the current in the ring. As  $d\sigma_1$  is in the same direction as the curves  $C_p$ ,  $I_1$  is positive if the current flows in the same sense as  $C_s$ , otherwise it is negative. Equation 12-16 is transformed in this way into

$$\frac{1}{2} \int (\mathbf{H} \cdot \mathbf{H}) d\tau = \frac{S_c I_1}{2c} - \frac{1}{2c} \int (\mathbf{A} \cdot \mathbf{H}) d\tau \quad (12-19)$$

On the other hand, the magnetic energy of the field is, by eqs. 5-8 and 3-2

$$\frac{1}{2} \int \mathbf{H}^2 d\tau = \frac{1}{2} \int (\mathbf{H} \cdot \mathbf{H}) d\tau - \frac{1}{2} \int (\mathbf{H} \cdot \mathbf{M}) d\tau$$

$I_0$  is the imaginary part of the complex function  $\ln(x + iy)$ .

where the suffix  $P$  indicates that the integral extends over the whole of space, whereas the suffix  $P$  indicates that it extends over only the permanent magnets in the field. By eq. 12-1 and the rule 5-1 we have

$$\frac{1}{2} \int (\mathbf{H} \cdot \mathbf{H}) d\tau = \frac{1}{2} \int (\mathbf{H} \cdot \operatorname{curl} \mathbf{A}) d\tau = \frac{1}{2} \int (\mathbf{A} \cdot \operatorname{curl} \mathbf{H}) d\tau - \frac{1}{2} \int ((\mathbf{A} \times \mathbf{H}) \cdot d\sigma)$$

The surface integral vanishes over the sphere at infinity because there  $\mathbf{H}$  behaves like  $R^{-3}$ . The tangential components of  $\mathbf{H}$  and  $\mathbf{A}$  are continuous at surfaces of discontinuity, therefore the normal component of  $(\mathbf{A} \times \mathbf{H})$  which depends only on these tangential components is also continuous and does not contribute anything. Therefore

$$\frac{1}{2} \int \mu \mathbf{H}^2 d\tau = \frac{1}{2c} \int (\mathbf{A} \cdot \mathbf{A}) d\tau - \frac{1}{2} \int (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (12-20)$$

The field is produced by the ohmic current in the normally conducting coils together with the corresponding supercurrent in the superconductor, and also by any persistent current that may be present. We designate the coils by the suffix  $S$  under the integral sign. Splitting up the right-hand side of eq. 12-19 in this way yields:

$$\frac{1}{2} \int \mu \mathbf{H}^2 d\tau = \frac{1}{2c} \int (\mathbf{A} \cdot \mathbf{A}) d\tau + \frac{1}{2c} \int (\mathbf{A} \cdot \mathbf{V}) d\tau - \frac{1}{2} \int (\mathbf{H} \cdot \mathbf{M}) d\tau$$

Adding this equation to 12-19 we get

$$\frac{1}{2} \int (\mathbf{I} \cdot \mathbf{I}) d\tau + \frac{1}{2} \int \mu \mathbf{H}^2 d\tau = \frac{1}{2c} \left\{ S_c I_1 + \int (\mathbf{A} \cdot \mathbf{V}) d\tau \right\} - \frac{1}{2} \int (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (12-21)$$

According to eq. 5-8 the left-hand side of this is the total energy of the field  $U$ , which is necessarily positive or zero, the latter only if  $\mathbf{I} = 0$  and  $\mathbf{H} = 0$  everywhere. This equation implies the following theorem.

The "period"  $S_c$  of the superconducting potential in the ring, together with the ohmic currents and the permanent magnets determine uniquely the magnetic field of the supercurrent. This is because if we assume two different fields with the same ohmic currents and permanent magnets, the difference between the two fields also satisfies the differential equations of the London theory. Therefore eq. 12-21 may be expressed in terms of this difference, but the right-hand side vanishes by hypothesis.

For a singly connected superconductor the first term of the right-hand side is missing; it is therefore current free in the absence of external excitation; otherwise the apparatus producing the field determines the situation uniquely. This theorem also guarantees the uniqueness of the solution of those examples in Chaps. 10 and 11 which are not covered already by the uniqueness theorems of eqs. 7-4. Equation 12-21 admits the possibility of an independent persistent current in a ring, but otherwise the ring is determined in all details by specifying its  $S_c$ . For instance its

magnetic moment is equal to  $S_C P$  where  $P$  is a vectorial factor depending only on the geometry of the ring and the intensive functions of position  $\alpha_p$ . The magnetic moment can only assume two opposite directions; the sign of  $S_C$  decides which one. In so far as the persistent current alone is exciting the field, the direction of the current is such as to make  $S_C I'$  positive. If in Fig. 12-1 the current flows in the positive sense, assigned to all curves  $C_1$  in the ring, then the magnetic lines of force, assigned to all the ring have the direction of  $d\phi$ , i. e., they come toward the reader. If we place a ring carrying a persistent current in an external magnetic field, then an induced current is superposed on the original current. In spite of the constancy of  $S_C$  the resulting current strength  $I$  can become zero or even reverse in sign.

Let a normally conducting specimen be placed in a magnetic field and then cooled until it becomes superconducting; then there is a considerable flux of induction through the ring but no current, or only a very weak current. Which of these possibilities is realized depends upon the detailed course of events during the cooling process and is difficult to determine. Switching off the magnetic field does not change the flux, but the current increases to the strength determined by the total flux and the form of the specimen. This is a common method of producing persistent currents.

To generalize eq. 12-21 for an "n"-ply connected superconductor we replace the one term  $S_C I$  by  $(n-1)$  terms of the same kind. The corresponding statement applies if several separate superconductors are present in the field.

Because of its magnetic moment every superconductor that has a persistent current must experience a torque in a homogeneous magnetic field in addition to that due to field deformation caused by the shape of the specimen.<sup>4</sup>

Suppose the superconductors to be rings formed by circles rotated around  $(I)$ . Let us assume two superconductors, both with persistent currents  $I$  and  $I'$ , to be moving relative to each other. The forces between them perform work, and/or lack of any other source of energy, at the expense of the energy  $S_C I + S_C I'$ . Because  $S_C$  and  $S_C'$  are constants according to eq. 12-14 a change of energy is only possible by a change of the strengths of the currents.

<sup>4</sup>Why is it that there is in the theory of ohmic currents and their magnetic fields

no uniqueness theorem corresponding to eq. 12-21? This is because in this case the

equation of current distribution is satisfied uniquely by electrodynamics and because

after solving this problem the magnetic field can be deduced unambiguously from

the current density. It is impossible to separate the problem of the superconductor

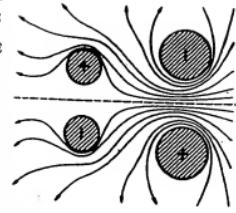


Fig. 12-4. Two superconducting rings with magnetic field lines.

current  $I$  flow in the first ring, but zero current in the second one. Let the rings now be brought together. The resulting lines of force are then sketched diagrammatically in the figure. If the current  $I$  flows away from the reader on the right-hand side (at the minus sign), then the current in the second ring flows toward the reader on the right-hand side. This follows from the rule (Chap. 7 (6)) that inner normal of the conductor, current, and magnetic field form a right-handed system. The antiparallel currents  $I_1$  and  $I_2$  repel each other; bringing the rings together requires the performance of work and produces an increase of the field energy  $S_C I^2$ , and thus an increase of  $I$ . However  $I'_1$  is also increased because the lines of force crowd together near the second ring and create a greater field strength the smaller the distance.

If a current  $I''$  is initially flowing in the second ring when at infinite separation, then the current  $I'' - I$  flows at the smaller distance, and there is attraction or repulsion depending on whether this expression is positive or negative. We have a stable equilibrium, at least with respect to motion along the axis, because a further approach leads to repulsion, and increase of distance to attraction. For example, in Justin's persistent current electromagnet the current strength decreases when it is attracting iron and the flux of induction  $S_C$  remains constant (Chap. [10]).

(f) A famous experiment performed in 1924 is in apparent contradiction to this argument. Kammerling-Onnes excited a persistent current in a hollow sphere of lead and so apparently in a singly connected region. He produced the current by the usual method of bringing the specimen, while at a higher temperature, into magnetic field and then cooling it to become superconducting. The sphere showed a magnetic moment after removing the field and experienced the corresponding torque in any external field. This great investigator concluded that the paths of the current could not be displaced in the superconducting body. If they could be, the forces exerted by the external field would be unable to move the sphere because it has no preferential direction.

From later experience the following explanation can be given for the above observation. The cooling of the hollow sphere immersed in liquid helium did not proceed everywhere with the same speed. At first one or may be several annular zones became superconducting while the rest of the sphere remained normal. The paths of the current could not be displaced in the superconducting body. If they could be, the forces exerted by the external field would be unable to move the sphere because it has no preferential direction.

<sup>4</sup>H. Kammerling-Onnes, *Commun. Leiden Supplément*, 69a, (1924).

the sphere remained normal. With the approach of temperature equilibrium the whole sphere had not become superconducting; instead, after the first zone had once trapped a certain amount of flux, the latter remained unchanged in the nonsuperconducting remainder of the sphere which stayed in the intermediate state (Chap. 19). With increasing concentration of the lines of force of the annular ring of superconducting material grew and the cross section of the normal material decreased, the field strength increased finally beyond the critical value  $H_c$  in the rest of the sphere and so prevented the complete establishment of the superconducting state.

Actually therefore the supercurrent was flowing in one of its several rings. Its magnetic moment was attached rigidly to this ring, and therefore also to the sphere, so the latter was forced to orient itself in an external field. This follows inevitably from the uniqueness theorem. However, even though Kamerlingh-Onnes failed to interpret his experiments, his question whether the current lines are displaced in a superconductor under the influence of an external magnetic field is still perfectly legitimate. This is discussed in Chap. 13.

(b) In the examples discussed in the last paragraph and in section (d) it was assumed that no ohmic current was supplied to the doubly connected superconductor from outside. But now let us imagine that at two points  $a$  and  $b$  on the surface of the superconductor, normally conducting wires are soldered through which a current  $I$  is supplied, entering at  $a$  and leaving at  $b$ , see Fig. 12-5. The ohmic current is distributed through the superconductor with a current  $I'$  flowing in the path that goes from  $a$  to  $b$  in the same direction as the "sense" of the ring, (which we arbitrarily choose for all from "2" to "1"), and a current  $I''$  in the other path. We regard both currents as positive if they are flowing from  $a$  to  $b$ . However, we know from Chap. 2 that one of them can be negative. This is true particularly if this persistent current is superimposed on the supplied current. In general

$$I' + I'' = I$$

This modified assumption does not alter eq. 12-10. Therefore eqs. 12-11 and 12-15 together with the theorems derived from them remain valid. But the integral on the right-hand side of eq. 12-16

$$\int (\mathbf{H} \cdot \nabla \mathbf{grad} \psi) d\tau = - \int \psi (\mathbf{H} \cdot d\tau)$$

acquires another value because it is no longer true that  $\mathbf{v} = 0$  everywhere over the surface. Suppose the cut that contributes to the integral is made first in the branch carrying the current  $I'$ ; this cut may be called  $'Q'$  and the function  $\psi'$  for this case will be written  $\psi'$ . The integral then becomes

$$-\frac{1}{2}(\psi_s - \psi'_s) I + S_c I'$$

If we displace the cut to the other branch and call it  $Q''$ , and the corresponding function  $\psi''$ , the surface integral becomes in the same way

$$-(\psi_s - \psi''_s) I + (\psi' - \psi'') I - S_c I''$$

Here  $I''$  has a minus sign because a positive  $I''$  has, by hypothesis, a direction opposite to the sense of the ring. The two values are equal because their difference

$$[(\psi_s - \psi'_s) - (\psi_s - \psi''_s)] I - (I' + I'') S_c = 0$$

This can be seen in the simplest way from eq. 12-22 by making use of the undetermined additive constant in the definition of  $\psi$  to make  $\psi' = \psi''$ . In this case  $\psi$  and  $\psi''$  are equal throughout the whole singly shaded region in Fig. 12-5 between the two cuts that enclose the point  $a$ , whereas in the other cross-hatched area, between the two cuts enclosing the point  $b$  we have  $\psi'' = \psi' = S_c$ . Equation 12-21 is now replaced either by

$$\frac{1}{2} \int (\mathbf{v} \cdot \mathbf{Q}) d\tau + \frac{1}{2} \int \mu \mathbf{H}^* d\tau =$$

$$-\frac{1}{2c} \left[ (\psi_s - \psi'_s) I + S_c I' \right] + \int (\mathbf{A} \cdot \mathbf{v}) d\tau - \frac{1}{2} \int (\mathbf{H} \cdot \mathbf{N}) d\tau \quad (12-23)$$

or by

$$\frac{1}{2} \int (\mathbf{v} \cdot \mathbf{Q}) d\tau + \frac{1}{2} \int \mu \mathbf{H}^* d\tau =$$

$$\frac{1}{2c} \left[ (\psi_s - \psi''_s) I - S_c I'' \right] + \int (\mathbf{A} \cdot \mathbf{v}) d\tau - \frac{1}{2} \int (\mathbf{H} \cdot \mathbf{M}) d\tau$$

the term containing  $S_c$  has the positive or negative sign if the current is in the positive sense  $I'$  or the negative sense  $I''$ , respectively. This agrees with the sign of the corresponding term in eq. 12-21.

This alteration does not affect the uniqueness theorem which we linked with eq. 12-21 because the current  $I$  supplied to the superconductor belongs to the ohmic currents of the external field. Also  $I$  becomes zero for the same ohmic currents and the same permanent magnets.

"Period"  $S_c$  the same ohmic currents and the same permanent magnets. (i) Considered as the source of its field, a persistent current has, according to eq. 12-21, only the energy  $U = S_c I_c$ . However,  $S_c$  is proportional to  $I$ , and we may write

$$\frac{S_c}{c} = \rho^* I_r. \quad (12-24)$$

and we see from the equation

$$U = \frac{1}{2} \rho^{\mu} I r^2 \quad (12-25)$$

that  $\rho^{\mu}$  is the coefficient of self-induction of the superconducting ring. It differs from the self-induction for an ohmic current in that in  $U$  and therefore also in  $\rho^{\mu}$  there is a positive term due to the energy of the supercurrent. However, this term is usually quite insignificant compared with the magnetic energy, because the superconductivity occurs for the most part only in thin layers where, due to the continuity of the components of  $H$ , most of the energy density is of the same order of magnitude as in adjoining parts of the outside space (see eq. 7-7'). This positive contribution is annulled in thick specimens by the far greater negative contribution from the expulsion of the field.<sup>6</sup> This idea can be carried through quantitatively only for special cases because the external magnetic field outside a superconductor is generally different from that for an ohmic conductor. From eqs. 12-14 and 12-24 it follows that for a thick superconductor the coefficient of self-induction is equal to the flux through the circuit divided by the velocity of light  $c$  and the current strength. For thin superconductors there is a correction according to eq. 12-11. It is well known that this theorem does not hold for normal conductors, because it is then impossible to define the flux through its own current circuit if it is considered infinitely thin, the flux is no longer finite. If there are ohmic currents of strength  $I'$  present in addition to the persistent current, we get

$$S_C = \rho^{\mu} I r + \sum_i \rho^{\mu} I' r_i$$

a linear function of all the current strengths. Furthermore, because the vector potential  $A$  is a linear sum of all the contributions from the separate currents, eq. 12-21 gives for the field energy, omitting the magnetic contribution,

$$U = \frac{1}{2} \sum_i \rho^{\mu} I_i r_i$$

This summation is extended over all the ohmic currents as well as the persistent current. The coefficients of induction between the persistent current and the ohmic currents are also affected by the energy of the supercurrent in the same way as the self-induction  $\rho^{\mu}$ . Beyond this we can say nothing without further information about the effect of the expulsion of the field.

<sup>6</sup> However, in a cable with the return path formed by its shell at a small distance from the inner conductor, supposing the shell to be superconducting, the superconductivity energy could be responsible for almost one-half of the coefficient of self-induction.

With regard to the other coefficients, the self-induction and the mutual inductions between the ohmic currents are also affected by the presence of the superconductor, just as they depend on the magnetic permeability in their neighborhood. One method for measuring the penetration depth  $\beta=1$  and the constant  $\lambda$  is based on this fact. It was devised by Casimir,<sup>7</sup> and used with success by Laermann and Shoenberg,<sup>8</sup> although not absolute, it gives the dependence on temperature. A long solenoid is wound tightly around a superconducting cylinder and a shorter induction coil is wound tightly around its center; their mutual induction is measured. The greater the penetration depth, the greater the flux of induction through the measuring coil due to the long solenoid, and so the greater their mutual induction. Two different specimens of mercury gave slightly different results in this experiment, and this is a reminder of the fact that the constant  $\lambda$  is really a tensor.

### CHAPTER 15

#### The Maxwell and London Stresses

(a) Kamerlingh-Onnes in 1924 raised the question whether the track of the supercurrent could be displaced in the superconductor under the influence of an external magnetic field [see Chap. 12 (8)]. He started from the assumption that in any case in the steady state the carriers of the supercurrent do not experience any forces due to the material itself, i. e., to the atoms and the carriers of the ohmic current, for otherwise persistent currents would be impossible. His question was, however, inconsequential in so far as the supercurrent already has its own magnetic field, so that the problem exists even before any external field enters the picture. Our present ideas about the current distribution had not been developed in 1924. We now have a clear picture of the current concentration in the protecting layer and we know that the current, magnetic field, and the inner normal force to the surface form a right-handed system (Chap. 7), and therefore that the force per unit volume  $\frac{1}{2} (I \times H)$  due to its own magnetic field is directed toward the interior of the superconductor (current, field, and force also form a right-handed system). We may therefore raise the question: Why does the magnetic field not push the current into the interior? How can the current in the thin protecting layer have any stability at all?

Another question is intimately connected with this. A rod carrying a supercurrent  $I$  and located in a magnetic field  $H$  perpendicular to the axis

of the cylinder, experiences a force  $\frac{1}{2} I H$  per unit length. Upon what does this force act? If the supercurrent mechanism experiences no force

<sup>7</sup> H. G. B. Casimir, *Physica*, 7, 887 (1940).

<sup>8</sup> E. Laermann and D. Shoenberg, *Nature*, 160, 747 (1948).

due to the material, neither can it exert force on the material: action and reaction must be equal. And yet the force due to the magnetic field certainly has to act first on the supercurrent mechanism, and through this somehow on the rod.

The answer can only be that the forces act on the material discontinuity at the surface. It is there that the interaction between matter and the supercurrent carriers must be located, and not in the interior. If such forces were not present even at the surface, the carriers would be able to escape from the metal, which certainly does not happen. The theory answers all these questions in terms of the London stresses. The force ordinarily exerted by the field can be calculated from the divergence of the Maxwell stresses, which are defined in terms of the electric and magnetic fields; similarly the London stresses, which are dependent only on the supercurrent, take care of the force exerted by the magnetic field on the supercurrent mechanism, and in fact locate it at the surface instead of throughout the body of the material. The supercurrent hangs as it were from the surface like a curtain, the magnetic field of the current corresponds to the weight of the curtain, the London stresses correspond to the elastic forces holding the curtain to its curtain rod and prevent it from falling into the interior. This is how we can answer Kammerling-Onnes' question.

The point therefore is to find a stress tensor that depends only on the current density  $\mathbf{J}$  and  $\mathbf{H}$ , that has a divergence that everywhere just compensates the force resulting from the Maxwell stresses in the magnetic field.<sup>1</sup> London's fundamental equations IX and X are needed to carry this through mathematically. They enter as the necessary and sufficient conditions for the system of London stresses to just compensate the Maxwell forces. The whole current distribution is fixed by this equilibrium condition. We regard the fact that it makes such a compensation possible as inherently the strongest point in favor of the theory.

This compensation is not entirely necessary for inhomogeneous superconductors or non-stationary currents. The discussion of the general equation 13-10 actually leads to completely new points of view.

(b) To begin with we define nine quantities in terms of two arbitrary vector functions of position  $\mathbf{P}$  and  $\mathbf{Q}$ :

$$\Theta_{\alpha\beta}(\mathbf{P}, \mathbf{Q}) = \mathbf{P}_\alpha \mathbf{Q}_\beta - \frac{1}{2} \delta_{\alpha\beta} \sum_i \mathbf{P}_i \mathbf{Q}_i \quad (\alpha, \beta = 1, 2, 3) \quad (13-1)$$

They form the components of a tensor of the second rank because the two parts  $\mathbf{P}_\alpha \mathbf{Q}_\beta$  and  $\frac{1}{2} \delta_{\alpha\beta} \sum_i \mathbf{P}_i \mathbf{Q}_i$  are each tensors themselves.<sup>2</sup> Written in greater detail the definition 13-1 reads:

$$\Theta_{11}(\mathbf{P}, \mathbf{Q}) = \frac{1}{2} (\mathbf{P}_1 \mathbf{Q}_1 - \mathbf{P}_2 \mathbf{Q}_2 - \mathbf{P}_3 \mathbf{Q}_3) \quad (13-2)$$

$$\Theta_{12} = \mathbf{P}_1 \mathbf{Q}_2 - \mathbf{P}_2 \mathbf{Q}_1, \quad \Theta_{13} = \mathbf{P}_1 \mathbf{Q}_3 - \mathbf{P}_3 \mathbf{Q}_1, \text{ etc.} \quad (13-3)$$

<sup>1</sup> As we later put  $-\operatorname{div} \Theta$  equal to the force acting on the material we have to regard a positive  $\Theta_{\alpha\beta}$  as a pressure, a negative one as a tension.  
<sup>2</sup>  $\delta_{\alpha\beta} = 1$  for  $\alpha = \beta$ , otherwise zero.

We now form the divergence of this tensor, i. e., the vector of which the  $x_1$  component is<sup>3</sup>

$$\operatorname{div}_1 \Theta(\mathbf{P}, \mathbf{Q}) = \frac{\partial \Theta_{11}}{\partial x_1} + \frac{\partial \Theta_{12}}{\partial x_2} + \frac{\partial \Theta_{13}}{\partial x_3} \quad (13-5)$$

Carrying through the calculation yields

$$\operatorname{div}_1 \Theta(\mathbf{P}, \mathbf{Q}) = \mathbf{Q}_1 \operatorname{div} \mathbf{P} - [\mathbf{P} \times \operatorname{curl} \mathbf{Q}]_1 + \frac{1}{2} \left( \sum_y \frac{\partial \mathbf{P}_y}{\partial x_1} - \sum_z \mathbf{Q}_y \frac{\partial \mathbf{P}_z}{\partial x_1} \right) \quad (13-6)$$

Now we set  $\mathbf{P} = \mathbf{l}$ ,  $\mathbf{Q} = \mathbf{G}$ , i. e.,  $\mathbf{Q}_y = \frac{\lambda_{\alpha\beta}}{\rho} \mathbf{l}_{\alpha\beta}$  (see eq. VIII Chap. 3); then because of the symmetry relations 3-3 ( $\lambda_{\alpha\beta} = \lambda_{\beta\alpha}$ ), the two sums cancel each other, at least if the  $\lambda_{\alpha\beta}$  are independent of  $x_\alpha$ . Otherwise there remains a term:

$$\frac{1}{2} \sum_{ab} \mathbf{l}_a \cdot \mathbf{l}_b \frac{\partial \lambda_{ab}}{\partial x_1} \quad (13-7)$$

By writing the tensor of third rank with components  $\partial \lambda_{ab}/\partial x_1$  as  $\nabla(\lambda_{ab})$ , the following vector equation results:

$$\operatorname{div} \Theta(\mathbf{l}, \mathbf{G}) = \mathbf{G} \operatorname{div} \mathbf{l} - [\mathbf{l} \times \operatorname{curl} \mathbf{G}] + \frac{1}{2} \sum_{ab} \mathbf{l}_a \cdot \mathbf{l}_b \nabla(\lambda_{ab}) \quad (13-8)$$

Now we use the continuity equation VII and the fundamental equation X to obtain

$$\operatorname{div} \Theta(\mathbf{l}, \mathbf{G}) = -\mathbf{G} \frac{\partial \rho^*}{\partial \mathbf{l}} + \frac{1}{c} [\mathbf{l} \times \mathbf{H}] + \frac{1}{2} \sum_{ab} \mathbf{l}_a \cdot \mathbf{l}_b \nabla(\lambda_{ab}) \quad (13-9)$$

Finally remembering IX we write

$$-\mathbf{G} \frac{\partial \rho^*}{\partial \mathbf{l}} = -\frac{\partial}{\partial \mathbf{l}} (\rho^* \mathbf{G}) + \rho^* \frac{\partial \mathbf{G}}{\partial \mathbf{l}} = -\frac{\partial}{\partial \mathbf{l}} (\rho^* \mathbf{G}) + \rho^* \mathbf{F}_l$$

and find in this way that

$$\operatorname{div} \Theta(\mathbf{l}, \mathbf{G}) = \rho^* \mathbf{E} + \frac{1}{c} [\mathbf{l} \times \mathbf{H}] + \frac{1}{2} \sum_{ab} \mathbf{l}_a \cdot \mathbf{l}_b \nabla(\lambda_{ab}) - \frac{\partial}{\partial \mathbf{l}} (\rho^* \mathbf{G}) \quad (13-7)$$

On the other hand, if we form the Maxwell stress tensors  $T(\mathbf{E})$  and  $T(\mathbf{H})$  for the interior of the superconductor where we do not need to distinguish between D and E or between H and H<sub>1</sub>, we have

$$T(\mathbf{E}) = -\Theta(\mathbf{E}, \mathbf{E}), \quad T(\mathbf{H}) = -\Theta(\mathbf{H}, \mathbf{H}) \quad (13-8)$$

Remembering the Maxwell equations I<sub>1</sub> and IV<sub>1</sub>, it follows from 13-4 that

$$-\operatorname{div}(T(\mathbf{E}) + T(\mathbf{H})) = \operatorname{div} \mathbf{E} - [\mathbf{E} \times \operatorname{curl} \mathbf{E}] + \mathbf{H} \operatorname{div} \mathbf{H} - [\mathbf{H} \times \operatorname{curl} \mathbf{H}] \\ = \rho \mathbf{E} + \frac{1}{c} [\mathbf{l} \times \mathbf{H}] - \frac{1}{c} [\mathbf{E} \times \mathbf{H}] \quad (13-9)$$

<sup>3</sup> See previous footnote.

Here  $\rho$  is the total density  $\rho^0 + \rho'$ ,  $I$  the total current  $I^0 + I'$ . Subtracting from eq. 13-7 yields

$$-\operatorname{div} [T(E) + T(H) + \Theta(I, Q)] = \rho^0 E + \frac{1}{c} [I^0 \times H] - \frac{1}{2} \sum_{ab} I_a I_b P^a P^b / \omega_0 + \frac{\partial}{\partial t} \{ [E \times H] + \rho' Q \} \quad (13-10)$$

This equation constitutes the momentum law.

In the stationary state  $E$  and  $H$  vanish (Chap. 7), and for the homogeneous field the double sum vanishes. In the stationary state, the Maxwell stresses of the magnetic field and the London stresses of the supercurrent result in no net force on the interior of a homogeneous superconductor, as was required. The symmetry of the tensor  $\lambda^{ab}$  is found to be a necessary and sufficient condition for this. In a time-dependent field the ohmic current mechanism exerts the force  $\rho^0 E + I^0 [I^0 \times H]$ . Per unit volume, it serves to change the mechanical momentum density. Moreover, the forces due to the three stress tensors produce an increase in the well-known electromagnetic momentum  $(1/c) [E \times H]$  and of the momentum density of the supercurrent  $\rho' Q$ . (This is why we have called  $Q$  the supermomentum.) Discussion of the double sum in eq. 13-10 is deferred until later. This also shows why we were not permitted to put the superconducting charge density  $\rho'$  equal to zero even in the stationary state where  $\rho$  is zero (see Chaps. 5 and 6); the momentum  $\rho' Q$  is without doubt always present in the stationary current.

(c) The Maxwell stresses do not act on the surface of a superconductor except in the case not to be discussed here that the material immediately across the surface has a dielectric constant or a permeability differing from unity. As all the components of  $E$  and  $H$  are continuous across the boundary, according to the boundary conditions of Chap. 3(c), the tensors  $T(E)$  and  $T(H)$  have equal components on either side of the surface, and so have  $\Theta(I, Q)$  surface divergence.<sup>10</sup> However, the London tensor  $\Theta(I, Q)$  does have a surface divergence because the supercurrent ceases at the surface. Let  $P_{(0)s}$  be this negative surface divergence; its components are

$$P_{(0)s} = - \sum_p \theta_{ap} \cos(\mathbf{n}, \mathbf{x}_p) \quad (13-11)$$

Using the definition 13-1 and introducing the unit vector  $\mathbf{n}$  in the direction  $n$ , we can write vectorially

$$P_{(0)s} = -I_s Q + \frac{1}{2} (\mathbf{v} \cdot \mathbf{q}) n \quad (13-12)$$

$P_{(0)s}$  is the force exerted by the supercurrent on the surface per unit area. This is the only ponderomotive force exerted by the current.

Wherever there is no current entering (or leaving) across the surface,  $I_s = 0$ ; a tension  $\frac{1}{2} (I_s Q)$  acts toward the interior. At points where

current enters there is a tangential component of the force due to the first term in 13-7.

In cubic crystals,  $Q = \lambda^{11}$  has the same direction as  $\mathbf{i}$  everywhere. Then the current streamline is the only intrinsic direction and must be a principal axis of the tensor  $\Theta(I, Q)$ . As can be seen from the equations

$$\theta_{11} = \frac{1}{2} [I_1^4 - I_2^4 - I_3^4], \quad \theta_{22} = \theta_{33} = 2 I_1 I_2 \quad (13-13)$$

this tensor becomes symmetrical. Putting the  $x_1$  axis parallel to the current, the components  $\theta_{ab}$  with mixed suffixes vanish, and we get

$$\theta_{11} = \frac{1}{2} I_1 I^2, \quad \theta_{22} = \theta_{33} = -\frac{1}{2} I_1 I^2 \quad (13-14)$$

In this case therefore a pressure  $\frac{1}{2} \lambda^{11}$  acts along the current line, and an equal tension perpendicular to it. It manifests itself at the surface where  $I_s = 0$  as a tension  $\frac{1}{2} \lambda^{11}$  directed toward the interior. We can illustrate the meaning of the double sum in eq. 13-10 for the cubic crystal case where it reduces to

$$-\frac{1}{2} I^2 \operatorname{grad} \lambda \quad (13-15)$$

Where two superconductors with different  $\lambda$ 's make contact, the stresses give rise to a force on the boundary. In case the current crosses the boundary perpendicularly,  $(I_{11})_1 = (I_{11})_2$ , and eq. 13-15 gives the difference between the two pressures along the current lines:  $\frac{1}{2} \lambda_2^{11} (I_{11}^{(2)} - I_{11}^{(1)})$ . Where, however, the two currents flow parallel to the boundary,  $I_{11}(1)_1 = I_{11}(2)_1 = C$  according to eq. 13-9, and the integral of eq. 13-15 over the thickness of the boundary layer yields the difference between the two tensions:  $\frac{1}{2} C (I_{11}^{(2)} - I_{11}^{(1)})$ .

In all these cases the force given by eq. 13-15 is directed toward the better superconductor with the smaller  $\lambda$ .

(d) The stress system assumes a particularly simple form in the fully developed protective layer of a thick cubic crystal conductor. With the  $x$  axis of coordinates along the inner normal, eqs. 7-9 and 7-10 give

$$I_s = I_s = 0, \quad H_s = H_s = 0, \quad H_y = |I_s|, \quad H_x = 0. \quad (13-16)$$

Therefore in the direction of the pressure  $\frac{1}{2} H_s$  of the magnetic field and the tension  $\frac{1}{2} \lambda^{11}$  of the current cancel each other at every point. In the direction of the current, however, the pressure  $\frac{1}{2} H_s$  and  $\frac{1}{2} \lambda^{11}$  are equal and have to be added together, but because they do not depend on  $x$  they give rise to no resultant force, in agreement with eq. 13-10.

(e) To answer a question remaining from section (d) we now calculate from the London stresses the force exerted on a superconducting cylinder of cubic crystalline material carrying a current  $I$  in a transverse magnetic field  $H^0$ . Figure 13-1 represents a cross section of the cylinder, and if  $H^0$  is in the  $x$  direction, the current produced by this field flows toward the reader in a direction  $a$  and away from the reader in  $b$ . The current inward reader, the current at  $a$  is greater than that at  $b$ . The stronger inward

tension at  $a$  and its neighborhood results in a force from  $a$  toward  $b$ , in the  $y$  direction in the figure. This force, the current  $I$ , and the field  $H^0$  form a right-handed system as they should.

The numerical calculation can be carried out by the methods of Chap. 8 (a) and Chap. 10 (e). From Eq. 8-9 the density  $i$  of the current  $I$  at  $r = R$  is

$$i_{(1)} = \frac{(R I) J_0(\beta R)}{2\pi R^2 I_0'(\beta R)}$$

The current density due to the field  $H^0$  according to Eq. 10-16 is

$$i_{(2)} = \frac{i_e H^0 \sin \theta}{\sqrt{\lambda}} \frac{J_1(\beta R)}{I_0(\beta R)}$$

The inward tension therefore has the strength

$$\frac{1}{2} \lambda (I_{(1)} + I_{(2)})$$

If this is multiplied by  $-\sin \theta$ , we obtain its contribution to the total force on the surface  $K_y$ , the value of which is

$$K_y = -\frac{1}{2} R \lambda \int_{(1)}^{(2)} (I_{(1)} s + I_{(2)} s + 2 i_{(1)} i_{(2)}) \sin \theta d\theta$$

Because

$$\int_0^{2\pi} \sin \theta d\theta = 0 \quad \text{and} \quad \int_0^{2\pi} \sin^2 \theta d\theta = \pi, \quad \text{this reduces}$$

$$K_y = -R \lambda \int_0^{(2)} I_{(1)} s \sin \theta d\theta = \frac{I H^0}{c}$$

(1) An example of the tangential component of the force  $K$  would be given by a Barlow's wheel made of superconducting cubic crystal material.

This consists of a circular disk in a magnetic field parallel to its axis that is homogeneous in the absence of the field; current is supplied through the axis of the disk and is drawn off through a normal conductor at its perimeter. If the disk is thick compared with the penetration depth, the field is distorted by the Meissner effect and considerably increased at the periphery, while according to Chap. 7 (g) the field would penetrate a thin disk relatively undisturbed, assuming it still to be of cubic crystalline structure.

The above stresses act on the two circular faces of the disk. Because they are parallel to the axis they produce no angular momentum. However, near the point where the current leaves the disk there is a tangential current

$i_s$  flowing along the periphery which is proportional to  $H^0$  and protects the interior of the (thick) superconductor from the field. At the point where the current leaves, there is a tangential force  $G_{rs} = \lambda i_s i_s'$  that does produce angular momentum. The calculation shows that a thin disk the force has the same value as for a normal conductor, while with a thick disk it has the same direction but is much weaker.<sup>4</sup>

The reality of the Maxwell stresses in empty space is vouchsafed by the principle of relativity. In so far as the energy density is unchanged in all inertial systems connected by a Lorentz transformation, the same equality must be ascribed to the stress components that are transformed along with this energy density and form with it a "word tensor." It is difficult to believe that this does not also hold for the Maxwell stresses. However, it is not inconceivable that the London stresses are purely a convenient mathematical fiction. In what follows we assume the contrary.

(2) Because in the above examples the net force and the torque are acting on an essentially rigid body, we could have started from the external magnetic stresses  $T$  ( $H$ ) instead of from the London stresses in the interior; which stresses exist in the interior is of no importance for such a calculation so long as all the stress tensors are symmetrical.

In order to carry through this alternative, we recall the two well-known integral theorems of the tensor theory. It is possible by partial integration to transform certain volume integrals of an arbitrary asymmetrical tensor  $t_{ab}$  into surface integrals. Let  $n$  again mean the inner normal, then we have first

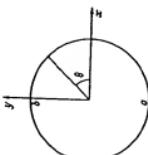
$$\int \left[ \frac{\partial t_{11}}{\partial x_1} + \frac{\partial t_{12}}{\partial x_2} + \frac{\partial t_{13}}{\partial x_3} \right] dt = - \int [t_{11} \cos(n \cdot x_1) + t_{12} \cos(n \cdot x_2) + t_{13} \cos(n \cdot x_3)] da \quad (13-16)$$

and secondly,

$$\begin{aligned} & \int \left\{ \left[ \frac{\partial t_{21}}{\partial x_1} + \frac{\partial t_{22}}{\partial x_2} + \frac{\partial t_{23}}{\partial x_3} \right] - x_3 \left( \frac{\partial t_{21}}{\partial x_1} + \frac{\partial t_{22}}{\partial x_2} + \frac{\partial t_{23}}{\partial x_3} \right) \right\} dt = \\ & = - \int \{ x_3 [t_{21} \cos(n \cdot x_1) + t_{22} \cos(n \cdot x_2) + t_{23} \cos(n \cdot x_3)] - x_3 [t_{11} \cos(n \cdot x_1) + \\ & + t_{12} \cos(n \cdot x_2) + t_{13} \cos(n \cdot x_3)] \} da + \int (t_{22} - t_{12}) dt \end{aligned} \quad (13-17)$$

<sup>4</sup>W. Heisenberg and M. V. Laue, Z. Physik, 184, 514 (1948). With regard to the present state of our knowledge about supercurrents and surface phenomena, one might perhaps doubt whether the torque is acting on the disk itself or on the normally conducting wire that leads the current out of the disk. The phenomenological theory described here cannot answer this question, but we could imagine the leads replicated by a cold emission from the periphery through the surrounding space where it could conceivably be decided experimentally whether or not the torque acts on the wire.

\* In this and subsequent formulas  $da$  is not a vector.



The force per unit area on any surface due to the tensor  $T(H)$  now has the components

$$F_{ss} = \sum_s T_{ss} \cos(\theta_{ss}) \quad (13-18)$$

which can be written together in vector form:<sup>4</sup>

$$\mathbf{F}_s = -\mathbf{H}_s \mathbf{H} + \mathbf{H}^s \mathbf{n} \quad (13-19)$$

( $n$  is again the unit vector normal).

The difference in sign between the right-hand sides of eqs. 13-18 and 13-11 is due to the fact that the Maxwell stresses we are discussing here lie outside the space element, whereas the London stresses are inside it. The resultant force on this element is, according to eq. 13-16,

$$-\int \operatorname{div} T(H) d\tau = \int F_s d\sigma \quad (13-20)$$

and the torque due to the Maxwell stresses is:

$$-\int [\mathbf{r} \times \operatorname{div} T(H)] d\tau = \int [\mathbf{r} \times \mathbf{F}_n] d\sigma \quad (13-21)^*$$

By using eq. 13-20 one can easily calculate from  $F_n$ , e. g., the force  $(1/\mu_0) H^s$  acting on the cylinder carrying a current in a magnetic field treated in [6].

We now want to find the conditions under which the net force and the torque due to the Maxwell stresses in the outside space coincide with the net force and the torque due to the London stresses in the interior. The volume integral for the Maxwell stresses on the right-hand side of eq. 13-17 vanishes because the tensor  $T(H) = -\theta(H, H)$  is symmetrical according to eq. 13-2. It also vanishes for the tensor  $\theta(H, Q)$  in a cubic crystalline superconductor, because in this case  $Q = \lambda I$ . Therefore integrating eq. 13-11 over the volume of the superconductor, using eqs. 13-16 and 13-17, we conclude that

$$-\int \operatorname{div} \theta(H, Q) d\tau = -\int K_s d\sigma \quad (13-22)$$

and

$$-\int [\mathbf{r} \times \operatorname{div} \theta(H, Q)] d\tau = -\int [\mathbf{r} \times K_s] d\sigma \quad (13-23)$$

For the homogeneous superconductor in a stationary state we have, according to eq. 13-10,  $\operatorname{div} T(H) = -\operatorname{div} \theta(H, Q)$ . Therefore

$$\int F_s d\sigma = \int K_s d\sigma, \quad \int [\mathbf{r} \times \mathbf{F}_s] d\sigma = \int [\mathbf{r} \times K_s] d\sigma \quad (13-24)$$

The net resultant force acting on an arbitrary superconductor can be calculated equally well either from the Maxwell stresses in the outside space or from the London stresses in the interior. The two methods give

\* Because according to eqs. 13-8 and 13-1,  $T_{ss}(H) = -H_s H_j + \frac{1}{2} \delta_{ss} H^2$ .

the same result for the torque of the force only if the superconductor is of cubic crystal material. This always is true, although the separate forces  $F_s$  and  $K_s$  may have the same value, namely,  $F_s = K_s = \frac{1}{2} H^2 n$ , only for thick superconductors (compare eqs. 13-12, 13-13, and 7-31) and where no current is entering or leaving the superconductor.

However, when in Chap. 17 we calculate the work performed by the magnetic field during an arbitrary displacement of the phase boundary between normal and superconducting material, we have to start from the forces  $K_s$  due to the London stresses, because they alone yield the actual force on every element of the surface.

(H) We still have to consider the term  $\int [f_{ss} - f_{ss}] d\tau$  in eq. 13-17 as applied to the tensor  $(V, G)$ . In the first place this equation, the other terms of which represent torques, shows that  $\theta_{ss} - \theta_{ss}$  is the  $s$  component of a polar vector. We therefore introduce the vectors  $\theta_{ss} = \theta_{ss} - \theta_{ss}$ ,

$$\theta_{ss} = \theta_{ss} - \theta_{ss}, \quad \theta_{ss} = \theta_{ss} - \theta_{ss}, \quad \theta_{ss} = \theta_{ss} - \theta_{ss}, \quad (13-25)$$

which according to eq. 13-2 we can also write vectorially as

$$\theta = (\mathbf{d} \times \mathbf{v}) \quad (13-26)$$

Equation 13-23 obviously has to be supplemented to read

$$-\int [\mathbf{r} \times \operatorname{div} \theta(H, Q)] d\tau = -\int [\mathbf{r} \times K_s] d\sigma + \int \theta d\tau \quad (13-27)$$

We can apply this equation not only to the whole volume of the superconductor but also to any part of it, provided only we keep in mind that in this case the forces  $K_s$  are not effective, but are completely compensated by the London stresses from outside the region of integration. Equation 13-27 therefore states: The London stresses in a noncubic crystal superconductor produce a torque  $\theta$  per unit volume. Because of the equality between action and reaction the material, in the stationary state, has to exert a torque  $\theta' = -\theta$  on the superconduction mechanism. This result at first seems most surprising.

In classical mechanics there are already cases where a torque is necessary to maintain uniform motion.

For example, a rigid body moving through liquid thrusts the latter to one side, in the absence of special symmetry conditions, and an impulse perpendicular to the component  $v$  associated with the velocity  $v$  is displaced along with the body, the motion of the body. As this impulse is changing by  $(v \times \mathbf{G})$  per unit time, where  $\mathbf{G}$  represents the momentum of the body, if a torque of this direction and magnitude did not act on the body it would not be able to persist in uniform motion. See Fig. 13-2.

Section (b) showed us that a momentum  $P$  per unit volume is

associated with the supercurrent. The concept of a velocity  $v$  of the super-



Fig. 13-2. The shaded area represents the vector product  $(V \times Q)$  per unit area, where  $V$  is the velocity of the supercurrent,  $Q$  is the angular momentum per unit time.

current is alien to the phenomenological theory. However, in so far as it has any meaning at all, it certainly has the value given by  $\rho' v = \mu'$ . Then the required torque per unit volume becomes

$$\theta' = [v \times \rho' Q] = [v \times G]$$

and this actually is equal to  $-6$ .

The combination of eqs. 13-27 and 13-28 gives for the whole superconductor

$$\int [r \times F_s] dr = \int [r \times K_s] dr + \int \theta' dr \quad (13-28)$$

instead of the second equation of 13-24. The torque due to the Maxwell stresses in outside space,  $\int [r \times F_s] dr$ , serves to increase the mechanical angular momentum of the superconductor from outside, i.e., the moment of all the forces acting on the superconductor from outside according to this equation is equal to the moment  $\int [r \times K_s] dr$ ;  $d\sigma$  according to this equation angular momentum is also imparted to the superconducting mechanism.

(i) The results of this chapter concerning ponderomotive forces and the torque due to the field are so important for the further development of the theory that we wish to confirm them in the next chapter by expressing them in terms of an electrodynamic potential, at least for the stationary case. We derive this potential itself by a plausible generalization of the usual potential of the Maxwell theory.

#### 14. THE ELECTRODYNAMIC POTENTIAL

first term is absent. The integration has to be extended over the whole space (as indicated by the suffix  $V$ ). In the term  $(M \cdot H)$  the integration is taken only over the volume of the permanent magnets, in the term  $\frac{1}{2} \mu' (i \cdot Q)$  only over the volume of the superconductor; these two volumes are mutually exclusive, and the observation that no ferromagnetics ever become superconducting is therefore significant for the following proof. Electric field vectors do not appear because of our assumption that at every instant the state is infinitesimally near to a stationary state.

Let the material displacement be  $u$ , a continuous vector function of position. The proof of the above theorem is effected as soon as we can express the decrease in potential in the form

$$-\partial V = \int \left\{ (K \cdot \dot{u}) + \frac{1}{4} (\theta \cdot \operatorname{curl} \dot{u}) \right\} dr \quad (14-2)$$

where  $K$  means the force per unit volume determined by the well-known electrodynamic laws, and  $\theta$  is the torque given by eq. 13-26. In other words we must show that the right-hand side of this expression is the work  $2A$  done by the field. The boundary conditions are that all material constants, including  $A_F$  and  $\mu$ , do not change their values at any material point, furthermore that the ohmic current flows through any material surface with the same strength  $\int J^0 ds'$  before and after the displacement, and also that the permanent magnetism  $/ M_n ds'$  remains unchanged. We shall therefore have

$$\partial \int A^0 ds' = 0, \quad \partial \int M_n ds' = 0 \quad (14-3)$$

We assume the condition of the constant ohmic current strength to be realized by arranging for suitable changes of the electrodynamic forces to compensate all changes of induction due to the displacements. We cannot introduce such a condition for the annular current in a superconductor. For this current is the potential period  $S$  (Chap. 12) and not the current strength that remains unchanged, and for the current density here we have eq. 12-10,

$$c G + A = \operatorname{grad} \varphi \quad (14-4)$$

(b) To formulate the assumptions under discussion mathematically, we use at first some well-known equations. If  $\delta u$  means the change of the parameter  $\mu$  at a material point,  $\delta \varphi$ , the change at a point fixed in space, the following relation holds:

$$\delta \varphi = \delta \mu + (\dot{u} \cdot \operatorname{grad} \mu) \quad (14-5)$$

As  $\delta \mu$  shall be zero, we have to put

$$\delta \varphi = -(\dot{u} \cdot \operatorname{grad} \mu) \quad (14-5)$$

Furthermore, the change of flux of an arbitrary vector through a material surface integrates to

$$\partial \int K_n ds' = \int (2K + \partial u \operatorname{div} K - \operatorname{curl} [\partial u \times K]) ds' \quad (14-6)$$

$\int ds'$ , in contrast to  $ds$ , is a surface element participating in the displacement.

#### CHAPTER 14

##### The Electrodynamic Potential

(a) We shall prove the following theorem with the unimportant restriction that only one superconductor is situated in the field, and the more important restriction that no ohmic current is supplied: In any quasi-stationary change of the field, occurring as a consequence of displacements of the field, the work  $\delta A$  performed by the field is equal to the decrease of the electrodynamic potential  $-\partial V$  defined by

$$V = \frac{S I}{c} - \left\{ \frac{1}{2} \mu' H^2 + (M \cdot H) + \frac{1}{2} (i \cdot Q) \right\} dr \quad (14-1)$$

As in Chap. 12,  $I$  is the current flowing in the superconductor when the latter is in the form of a ring,  $S$  is the time invariant period of the superconductor potential  $\psi$ , if the superconductor is singly connected the

<sup>1</sup>Compare Von Laue reference <sup>a</sup> and <sup>b</sup> in footnote 2, Chapter 3.

Therefore if we remember that here the stationary state means  $\operatorname{div} \mathbf{v} = 0$ , the conditions 14-3 yield

$$\partial M = -(\operatorname{div} M) \mathbf{u} + \operatorname{curl} [\mathbf{u} \times \mathbf{M}] \quad (14-6)$$

Although the above considerations are based on well-known theorems<sup>1</sup> we shall have to leave the proof of the next equation to the Appendix, namely that under the condition that the  $\lambda_{\alpha\beta}$  do not change at any material point, the changes  $\partial_{\alpha\beta} A$  at a fixed point in space satisfy the equation

$$\frac{1}{2} \sum_{\alpha\beta} \lambda_{\alpha\beta} \partial_{\alpha\beta} A_{\alpha\beta} = -\frac{1}{2} \sum_{\alpha\beta} \lambda_{\alpha\beta} \left( \partial_{\alpha} (\partial_{\beta} A_{\beta}) + \frac{1}{2} (\operatorname{curl} \mathbf{u} \cdot \{\mathbf{g} \times \mathbf{u}\}) \right) \quad (14-8)$$

It is obvious that throughout the superconductor

$$\operatorname{div} \mathbf{u} = 0 \quad (14-9)$$

$$\mathbf{u} \cdot \mathbf{u} = 0 \quad (14-10)$$

We take into account only one surface of discontinuity, namely the superconductor, and assume all other transitions to be continuous. In particular, the permanent magnetization  $M$  must go continuously as we move from the interior of a permanent magnet; the actual conditions there can be taken care of afterwards by going to the limit.

(c) We proceed to the proof of eq. 14-2. According to eq. 14-1 we have

$$-\partial V = -S \partial T + \frac{1}{c} \int \mu H^2 + (M \cdot H) + \frac{1}{2} (\mathbf{u} \cdot \mathbf{g}) \, d\tau$$

The right-hand side can be split into six terms of the following type:

$$-\partial V = \sum_{k=1}^6 \partial I_k - \frac{S}{c} \partial T$$

$$\partial I_1 = \int \mathbf{B} \cdot \partial \mathbf{H} \, d\tau$$

$$\partial I_4 = \int (H \cdot \partial M) \, d\tau$$

$$\partial I_3 = \frac{1}{2} \int H^2 \partial u \, d\tau \quad (14-11)$$

$$\partial I_4 = \int (\mathbf{g} \cdot \partial \mathbf{u}) \, d\tau$$

(14-11)

The first term vanishes because of eq. 14-9, and the surface makes no contribution because of eq. 14-10. But with a doubly connected body, a cut  $Q$  makes a contribution to the surface integral (compare eq. 12-17):

$$-\frac{1}{c} \oint \Psi \partial u \cdot d\sigma = \frac{1}{c} (\Psi_s - \Psi_L) \partial I = \frac{S}{c} \partial I$$

The sign is determined by the convention of Chap. 12 that a positive current flows through the cut in the direction  $2 \rightarrow 1$ . On the other hand, according to eqs. 14-6 and 12-1:

$$\frac{1}{c} \int (\mathbf{A} \cdot \partial \mathbf{u}) \, d\tau = \frac{1}{c} \int (\mathbf{A} \cdot \operatorname{curl} [\partial \mathbf{u} \times \mathbf{u}]) \, d\tau$$

$$= \frac{1}{c} \int (\mathbf{B} \cdot [\partial \mathbf{u} \times \mathbf{u}]) \, d\tau = \frac{1}{c} \int (\partial \mathbf{u} \cdot [\mathbf{u} \times \mathbf{B}]) \, d\tau$$

$$= \frac{1}{c} \int (\partial \mathbf{u} \cdot [\mathbf{u} \times \mathbf{B}]) \, d\tau + \int (\partial \mathbf{u} \cdot [\mathbf{u} \times \mathbf{B}]) \, d\tau \quad (14-12)$$

<sup>1</sup>See for example, Margenau and Murphy, Mathematics of Physics and Chemistry,

J. Van Nastriand, New York Chapter IV.

<sup>2</sup>As before the suffices  $s$  and  $L$  mean that the integration has to extend over the

superconductor or the permanent magnets respectively.

Again, using eqs. 13-26 and 14-6 we can rewrite

$$\partial I_s = \frac{1}{2} \int_0^r \left[ - \sum_{\alpha\beta} I_{\alpha} I_{\beta} \nabla^2 u_{\alpha\beta} + (\theta \cdot \operatorname{curl} u) \right] dr \quad (14-13)$$

Furthermore, by eq. 14-7, the theorem 5-1, and the fundamental equation 111 (remembering that the supercurrent  $\mu$ -1 is absent from the interior of the permanent magnets) we get

$$\begin{aligned} \partial I_s &= \int_0^r \left[ H \cdot (\operatorname{curl} [u \times M]) - \partial u \operatorname{div} M \right] dr \\ &= \int_0^r \left[ \frac{1}{c} ((\partial u \times M) \cdot \theta) - (\partial n \cdot H \operatorname{div} M) \right] dr \end{aligned} \quad (14-14)$$

Finally it follows from eq. 14-5 that

$$\partial I_s = -\frac{1}{2} \int_H^0 (\partial u \cdot \operatorname{grad} \mu) dr \quad (14-15)$$

By adding together eqs. 14-12 to 14-15 and using eq. 14-11 we obtain

$$-\partial V = \int_0^r \left[ (K \cdot u) + \frac{1}{2} (\theta \cdot \operatorname{curl} u) \right] dr \quad (14-16)$$

with the value of the vector  $K$  given by

$$K = \frac{1}{c} [(\theta \times \mu H) - H \operatorname{div} M - \frac{1}{2} H^2 \operatorname{grad} \mu - \frac{1}{2} \sum_{\alpha\beta} L_{\alpha} L_{\beta} \nabla^2 u] \quad (14-17)$$

This is the most general expression for the force exerted by a stationary magnetic field on a unit volume of matter. The first term represents the effect of the field on ohmic current. The second term is the effect on the density of permanent magnetic charges, the third is the effect on the third is the equally familiar force on regions of magnetic inhomogeneity, the fourth is the force on an inhomogeneous superconductor appearing in 13-10. Equations 14-16 and 14-17 contain therefore the proof of the latter statement that  $K = 0$  for the homogeneous superconductor, for then, by eq. 13-10  $K = 0$ .

(d) The theorem  $\partial A = -V$  comes from the Maxwell theory, and our definition 14-1 is simply a plausible extension of the definition of that theory. That we have arrived at exactly the same conclusions about the force  $K$  and the torque  $\theta$  by a line of reasoning that avoids the stress concept used in Chap. 13 on the argument about the London stresses seems to us to be a valuable confirmation of the essential truth of that theory. In addition, the observation that ferrimagnetics are unable to show super-

conductivity appears in a new light. Otherwise we would have found in eq. 14-14 another term

$$-\frac{1}{c} (\partial u \cdot \operatorname{curl} M) \quad (14-18)$$

also entering the expression for the force  $K$ , and this would have been in conflict with the fact that the existence of persistent currents demands that  $K$  be zero in a homogeneous superconductor. It seems as though permanent magnetism and superconductivity are mutually exclusive not only in the temperature ranges that happen to have been observed to date, but also fundamentally so.

(e) According to eq. 12-21 the total (available) energy of the field is

$$U = \frac{1}{2} \int_V (\mu H^2 + (\mu \cdot \theta)) dr = \frac{1}{2c} \left\{ S_I + \int_V (A \cdot \theta) dr \right\} - \frac{1}{2} \int_V (H \cdot M) dr \quad (14-19)$$

and so according to eq. 14-1,

$$V = \frac{1}{2c} \left[ S_I - \int_V (A \cdot \theta) dr \right] - \frac{1}{2} \int_V (H \cdot M) dr \quad (14-19)$$

If the field is produced only by an annular current  $I$  and permanent magnets, then  $V = U$  and the work  $\partial A = -\partial \theta$ . Conversely if the field is produced by ohmic currents,  $V = -U$  and  $\partial A = \partial U$ . The amount of work  $2 \partial A$  has then to be performed by the electrodynamic forces keeping the currents constant. This second point differs from the corresponding theorem of the Maxwell theory in that here superconductors (but with no annular currents) are permitted to be in the field.

Eliminating the term  $S_I / c$  from eq. 14-1 by means of eq. 12-19 we get a new expression for  $V$  of which we shall make immediate use, namely,

$$V = \frac{1}{c} \int_S (A \cdot \theta) dr + \frac{1}{2} \int_V (\theta \cdot \theta) dr - \int_V \left[ \frac{1}{2} \mu H^2 + (M \cdot H) \right] dr \quad (14-20)$$

(f) With the help of the potential  $V$  we shall now confirm the theorem of Chap. 13 (e) that the surface of the superconductor experiences an inward pull  $\frac{1}{2} (\theta \cdot Q)$  at all points where there is no current entering or leaving. For this purpose we ignore all displacements of matter, but displace the boundary between a superconducting and a chemically identical normal conducting phase in such a way that every surface element  $d\sigma$  suffers a displacement  $\delta$  normal to  $d\sigma$ . We take  $\theta_0$  to be positive if  $d\sigma$  moves toward the interior of the superconductor. If before the displacement the superconducting phase occupied the region  $s$ , afterwards it occupies the smaller region  $s'$ . A finite change therefore takes place in the layer  $s - s'$ ; supercurrent and supermomentum suddenly drop to zero. But as this layer is infinitely thin, the effects of this change at all other points in space is infinitesimal. In general  $n$  and  $\lambda_{so}$  do not change at all, and the same is true of the current density  $i^*$ , as we shall again keep the ohmic currents constant.

Starting from eq. 14-20 we split the change  $\partial V$  into five parts:

$$\begin{aligned} -\partial V &= \sum_{k=1}^5 \partial I_k, \\ \partial I_3 &= \int_{s'}^s (\mathbf{B} \cdot \partial \mathbf{H}) d\tau \\ \partial I_4 &= -\frac{1}{c} \int_s^{s'} \partial (\mathbf{A} \cdot \mathbf{v}) d\tau \\ \partial I_5 &= -\int_s^{s'} (\mathbf{G} \cdot \partial \mathbf{v}) d\tau \end{aligned} \quad (14-21)$$

The transformation proceeds as follows.

First, by eq.

$$\partial I_1 + \partial I_4 = -\frac{1}{c} \int_s^{s'} [\text{grad } \psi \cdot \partial \mathbf{v} + (\mathbf{v} \cdot \partial \mathbf{A})] d\tau$$

Then in spite of the infinitesimal  $\partial \mathbf{H}$  in the layer  $s \rightarrow s'$  by which the superconductor is reduced,  $\text{curl } \partial \mathbf{H} = -\partial \psi/c$  is finite, but  $\partial \mathbf{v} = 0$  everywhere; remembering this and using eq. 12-1 and the theorem 5-1 it follows that

$$\partial I_1 + \partial I_4 = \frac{1}{c} \int_s^{s'} (\mathbf{A} \cdot \partial \mathbf{v}) d\tau - \int_s^{s'} (\mathbf{A} \cdot \mathbf{v}) d\tau$$

Adding up  $\partial I_1$  to  $\partial I_4$ , the contributions of the layer  $s \rightarrow s'$  cancel. Again recalling eq. 14-4 there remains

$$\begin{aligned} \sum_{k=1}^5 \partial I_k &= \frac{1}{c} \int_s^{s'} [(\mathbf{A} - \text{grad } \psi) \cdot \partial \mathbf{v}] - (\mathbf{v} \cdot \partial \mathbf{A})] d\tau \\ &= -\int_s^{s'} (\mathbf{G} \cdot \partial \mathbf{v}) + \frac{1}{c} \int_s^{s'} (\mathbf{v} \cdot \partial \mathbf{A}) \end{aligned}$$

Now because of the symmetry of the tensor  $\lambda_{jk}$ , which enters once more as an important condition, we have

$$(\mathbf{G} \cdot \partial \mathbf{v}) = \sum_{ab} \lambda_{ab} \partial v^a = \sum_{ab} \lambda_{ab} \partial v^a = (\mathbf{v} \cdot \partial \mathbf{G})$$

and so from eqs. 14-4 and 14-9 and the constancy of  $S = \Psi_2 - \Psi_1$  we have

$$\begin{aligned} \sum_{k=1}^5 \partial I_k &= -\int_s^{s'} \left[ \mathbf{G} + \frac{\mathbf{A}}{c} \right] d\tau = -\frac{1}{c} \int_s^{s'} (\mathbf{v} \cdot \text{grad } \partial \psi) d\tau \\ &= -\frac{1}{c} \int_s^{s'} \psi \text{div } \mathbf{v} d\tau - J \partial (\Psi_2 - \Psi_1) = 0 \end{aligned} \quad (14-22)$$

There remains only the term  $\partial I_5$  in eq. 14-21 to be considered. In the layer  $s \rightarrow s'$  however, putting the volume element  $d\tau = d\sigma \cdot d\mathbf{v}$  we get by surface integration

$$\partial A_5 = -\partial V = \frac{1}{2} \int_s^{s'} (\mathbf{v} \cdot \mathbf{G}) d\sigma \cdot d\mathbf{v} \quad (14-23)$$

From this we deduce that  $\frac{1}{2} (\mathbf{v} \cdot \mathbf{G})$  is in fact the pull acting over the element  $d\sigma$  toward the interior of the superconductor.

(g) From the section (f) we can also make the following deduction. Given the relative positions of all bodies, the ohmic currents in them, the permanent magnetism, and the potential "period"  $S$  of all possible annular currents which may eventually appear, the stationary field adjusts itself to minimize the electrodynamic potential. If we disregard the displacements  $\partial \mathbf{u}$ , the integrals  $\partial I_4$  and  $\partial I_5$  in eq. 14-21 vanish for every virtual displacement of the field. Then eq. 14-22 gives

$$-\partial V = \sum_{k=1}^3 I_k = 0$$

If there is no ohmic current contributing to the field, then  $V = U$  according to section (d). The field adjusts itself to minimize the free energy. Also a persistent current by itself corresponds to a minimum of the free energy, of course with the boundary condition that the potential "period"  $S$  be given. Without such a condition the law of the minimum free energy cannot be proved.

### CHAPTER 15

#### Electric Waves in Superconductors with Cubic Crystal Structure

(d) According to the fundamental equation IX changes in time always produce an electric intensity  $\mathbf{E}$  in a superconductor; this in turn produces an ohmic current density  $\mathbf{j}$  in addition to the supercurrent, and also Joule heat according to the energy equation 5-6. This is the fundamental difference from static fields. To describe periodic waves, in what follows we always use complex expressions for the field strengths and all quantities linearly related to them. The waves will be designated by their angular frequency  $\omega$ , the numerical frequency  $\nu$  being  $\omega/2\pi$ . All the complex expressions are taken proportional to  $e^{i\omega t}$ .

It follows from VII-4 and IX for cubic crystal superconductors that

$$i^0 = \sigma \mathbf{E} = \omega \sigma \lambda V e^{i\omega t} \quad (15-1)$$

The supercurrent  $I$  is therefore lagging in phase by a quarter period behind the ohmic current and the field strength  $E$ . For the ratio of the amplitudes of the two waves we have

$$\frac{|I|}{|I|} = \omega \sigma \lambda$$

The greater  $\omega$  the greater the influence of  $|I|$  compared with  $|E|$ . The pure number  $\omega \sigma \lambda$  which we encounter here for the first time, will play a fundamental role in the ensuing calculations. The total current density is connected with the field strength by the relation

$$I = I^0 + I_s = E \omega \sigma \lambda - \frac{i}{\omega \lambda}$$

$$= E \frac{1 + i \omega \sigma \lambda}{\omega \lambda} \quad (15-2)$$

(b) Because of the inevitable production of Joule heat a progressive wave in a superconductor is damped just as in a normal conductor. For a plane polarized wave progressing in the  $z$  direction we write

$$P_x = E_0 \exp i \omega \left[ t - \frac{(x - z)}{c} \right], \quad P_y = E_1 = 0 \quad (15-4)$$

This satisfies the condition  $\operatorname{div} E = 0$ . According to the fundamental relation I it follows from this that

$$H_x = (n - i \kappa) E \exp i \omega \left[ t - \frac{(x - z)}{c} \right], \quad H_z = 0 \quad (15-5)$$

Consequently for waves in a superconductor the electric field strength, magnetic field strength, and direction of propagation are perpendicular to each other and form in this order a right-handed system, as is otherwise known to be the case. However, unlike the behavior of waves in a non-conductor,  $B$  and  $H$  do not oscillate in phase,  $E$  in general lagging in phase behind  $H$ . The amplitude decreases with increasing  $\omega$  by the factor  $e^{-\omega \lambda / c}$ , the energy density by  $e^{-2\omega \lambda / c}$ .  $\kappa$  is called the extinction coefficient,  $n$  the refractive index. Both are pure numbers and functions of  $\omega$ .

Inserting the value of  $E$  from eq. 15-4 in the telegrapher's equation  $W(E) = 0$  (compare Chap. 6), it is equally possible to insert the value of  $H$  from eq. 15-5 in  $W(H) = 0$ , because

$$W(E) = \partial E - \frac{1}{c^2} \frac{\partial B}{\partial t} - \frac{\sigma}{c^2} \frac{\partial B}{\partial z} - \frac{B}{\lambda^2} \quad (15-6)$$

one obtains the relation

$$(n - i \kappa)^2 = (\omega^2 \lambda^2 - 1 - i \omega \sigma \lambda).$$

The two real numbers  $n$  and  $\kappa$  are determined by

$$n^2 = \frac{1}{2} \frac{[(\omega^2 \lambda - 1) + \sqrt{(\omega^2 \lambda - 1)^2 + (\omega \sigma \lambda)^2}]}{[\omega^2 \lambda - 1 - (\omega^2 \lambda - 1) + \sqrt{(\omega^2 \lambda - 1)^2 + (\omega \sigma \lambda)^2}]} \quad (15-7)$$

If  $\omega^2 \lambda < 1$ , then  $n < \kappa$  and the wavelength  $2\pi c/\omega n$  is greater than the logarithmic damping factor, i. e., the distance in which the amplitude decreases by a factor  $e^{-\omega n}$  or 0.2%. No wave can actually develop at all under such circumstances. The field is quasistatic and its distribution in space is similar to a static one. If indeed  $\omega^2 \lambda \gg 1$  and  $\omega \sigma \lambda$  are small numbers, the following approximations hold:

$$n = \frac{1}{\sigma} \lambda^2 N, \quad \kappa = \frac{1}{\omega \lambda^2 N} \gg n \quad (15-8)$$

This can be seen in the simplest way by forming  $\kappa^2 = n^2$  and  $2\pi c/n$  from eq. 15-8, and comparing with eq. 15-6. Since in this case  $\omega \sigma \lambda \ll \beta$ , the amplitude decreases by the factor  $e^{-\omega n}$  just as in the static case.

On the other hand if  $\omega^2 \lambda > 1$ , then  $n > \kappa$  according to eq. 15-7, and the wavelength is therefore smaller than the logarithmic damping factor, so a whole series of waves is produced with only gradually decreasing amplitude. If indeed  $\omega^2 \lambda \gg 1$ , then the unity in the numerator of eq. 15-6 is negligible and we obtain the approximate values

$$n = 1 + \frac{(\omega \lambda)^2}{8}, \quad \kappa = \frac{\sigma}{2 \omega}, \quad (15-9)$$

which no longer depend on the superconductivity constant  $\lambda$ .

But such a condition can only be realized immediately below the transition temperature where  $\lambda$  is comparatively large. As soon as  $\lambda$  attains values of the order  $10^{-10}$  sec at somewhat lower temperatures, this condition is hardly possible any longer because, just as with the Maxwell theory, our theory cannot be regarded as valid for arbitrarily high frequencies. Let us consider the situation with mercury for which direct determinations of  $\beta$  and therefore also of  $\lambda$ , are available (see Chap. 1 and 12). Its conductivity  $\sigma$  at room temperatures is about  $10^{17}$  sec<sup>-1</sup> in Lorentz units ( $4\pi$  times its value in esu); it is about 500 times greater just above the transition temperature ( $10^{-1}$  sec). Therefore for  $\omega = 10^9$  per sec,  $\omega^2 \lambda = 10^{-11}$ , and  $\omega \sigma \lambda = 10^{-1}$  (short Hertzian waves, high radio frequency), and for  $\omega = 10^{14}$  per sec,  $\omega^2 \lambda = 10^{-5}$  and  $\omega \sigma \lambda = 10^4$  (infrared waves).

In the first case the ohmic current is about one hundred times smaller than the supercurrent; in the second case about one hundred times greater, according to eq. 15-2. In the first case the unity is the dominating term in the numerator of eq. 15-6; in the second case the number  $\omega \sigma \lambda$ , so that, just as for a normal conductor,

$$n - i \kappa = (1 - i) \sqrt{\frac{\sigma}{2 \omega}} \quad (15-10)$$

This indicates a complete identity between normal and superconductors for all optical processes. If only the supercurrent were to exist in the superconductor, then the superconductor would be transparent. The fact that there is no visible difference between the normal and the superconductor [Chap. 1 (d)] is a decisive proof of the existence of the ohmic current. For  $\omega = 10^4$  per sec. and  $\kappa = 10^{-4}$  per sec., eq. 15-10 gives  $n = \infty$  and  $x = 10^4$ . If  $\omega = 10^6$  per sec. then according to the above figures the conditions for the validity of eq. 15-8 are satisfied. The refractive index then has the order of magnitude  $10^9$  and the extinction coefficient  $10^8$  for radio frequency waves. The reflectivity of a specimen for a wave incident perpendicularly from empty space can be calculated from the well-known optical expression

$$\frac{(n-1)^2}{(n+1)^2 + k^2}$$

Under the present conditions this expression can be simplified to read

$$\frac{1 + \left(\frac{n-1}{x}\right)^2}{1 + \left(\frac{n+1}{x}\right)^2} = 1 - \frac{4n}{x} = 1 - 2\omega^2\sigma X^2. \quad (15-11)$$

Consequently that fraction of the energy given by the second term is absorbed in the superconductor and amounts, according to the figures used above, to about  $10^{-4}$ .

## CHAPTER 16

### The High-Frequency Resistance of Superconductors

(a) A direct current is distributed uniformly over the cross section of a normally conducting cylinder. Alternating current, however, is confined to a thin layer at the surface which becomes thinner with increasing frequency. The induction from the magnetic field of the alternating current itself protects the interior from the current. This is the 'skin effect' that exists in conductors of any form. In the superconductor a tendency to the same effect already exists even with the direct current because of the coupling between the supercurrent and the magnetic field expressed by eq. X. For high frequency alternating current this Meissner effect and the skin effect reinforce each other. The penetration depth of the field of such an alternating current is then smaller than for direct current in the super-

<sup>1</sup> See the discussion of eq. 16-18 for the meaning of the number  $\omega^2\sigma X^2$ .

conductor and smaller than for alternating current of the same frequency in a normal conductor. The skin effect eventually causes a very substantial decrease in the cross section that actually carries the current in a normal conductor and thus may cause a considerable increase of the resistance. A changing field, according to Chaps. 7 and 15, produces an average resistance in a superconductor. This resistance increases with increasing frequency not only because of the decrease of the conducting cross section, but also because of the increasing transfer of current from the supercurrent to the ohmic current in accordance with eq. 15-2. We shall describe this increase quantitatively for the cubic crystal material.

(b) First we have to determine the current density as a function of position. The telegrapher's equation of Chap. 6 for the total current density reads:

$$W(l) \equiv \mathcal{A}l - \frac{1}{c} \frac{\partial l}{\partial t} - \frac{\sigma}{c} \frac{\partial l}{\partial z} - \frac{1}{c} \frac{\partial^2 l}{\partial z^2} = 0$$

For periodic processes this becomes

$$\mathcal{A}l - \frac{1}{c} \frac{(\omega^2 + i\omega\sigma + k^2)}{c^2} l = 0$$

As we are confining ourselves to frequencies less than  $10^{10}$  per sec, the first term in the brackets is small compared with the second term when  $\sigma = 10^{18}$  per sec (see Chap. 16). We therefore neglect this term and write

$$\mathcal{A}l - k^2 l = 0$$

for superconductors where

$$k = \frac{(1 + i\omega\sigma\lambda)^{1/2}}{c \sqrt{2}}. \quad (16-1)$$

As the neglected term arises from the term  $2B/c^2$  in the fundamental equation II, it means we are neglecting the displacement current as compared with the conduction current. We complete the definition of  $k$  by choosing both its roots to be positive, i. e., both the real and the imaginary part of  $k$  shall be positive.

Going to the limit  $\lambda \rightarrow \infty$  leads to the normal conductor, because in this limit the last term of  $W(l)$  vanishes and instead of eq. 16-1 we have the differential equation

$$\mathcal{A}l - k_*^2 l = 0, \quad k_* = \frac{\sqrt{i\omega\sigma}}{c} \quad (\text{normal conductor}) \quad (16-2)$$

In both cases the boundary conditions are: div  $l = 0$ ,  $l$  is finite and continuous throughout the interior; and, because we are discussing quasi-stationary currents,  $l_z = 0$  at all surfaces; and finally integration of 1

The following relation exists between  $k$  and the refractive index and extinction coefficient:

$$k = i\omega \frac{(n - \kappa)}{c}$$

over any cross section yields the total current strength  $I = e^{\sigma t}$ . We treat  $I$  as a real quantity.

We obtain the magnetic field from the current density by the fundamental equation  $\nabla \times \mathbf{H} = \mathbf{J}$ , which, neglecting the displacement current, reads:

$$\text{curl } \mathbf{H} = \frac{1}{c} \quad (16-3)$$

In the external space we have the additional requirement that  $\mathbf{H}$  is the negative gradient of a potential obeying the equation  $\nabla^2 \varphi = 0$ . Besides requiring that  $\mathbf{H}$  be divergence free, the boundary conditions require also that  $\mathbf{H}$  be finite and continuous at the surface of the conductor, and vanish sufficiently rapidly at infinity. The calculations are carried out in the same way for both the superconductor and the normal conductor except that in the first case one has to use the  $\mathbf{k}$  of eq. 16-1 and in the other the  $\mathbf{k}_n$  of eq. 16-2.

We can also derive the electric field from the current density. For the normal conductor we use the fundamental equation VII 4,

$$\mathbf{E} = \frac{1}{\sigma} (\text{normal conductor}) \quad (16-4)$$

while for the superconductor we use eq. 15-3,

$$\mathbf{E} = \frac{e \omega \mathbf{l}}{(1 + i \omega \sigma)} \quad (\text{superconductor}) \quad (16-5)$$

We can therefore derive the field strength for the superconductor from that of the normal conductor by multiplying the latter by the factor

$$(1 + i \omega \sigma \lambda) \quad (16-6)$$

The last step consists of determining the Poynting energy current vector  $c(\mathbf{B} \times \mathbf{H})$ . The divergence of the time average of this vector gives the Joule heat per unit volume and unit time, and the integral  $c \int (\mathbf{B} \times \mathbf{H}) \cdot d\mathbf{v}$  is therefore the Joule heat developed in the enclosed volume per unit time. From the complex solutions for  $\mathbf{B}$  and  $\mathbf{H}$  obtained in the manner just described, we calculate the time average of the Joule heat as the real part of  $\frac{1}{2} c (\mathbf{B} \times \mathbf{H}^*)^2$ , where  $\mathbf{H}^*$  is the complex conjugate to  $\mathbf{H}$ .

<sup>1</sup>If one has the complex representations for two field quantities  $A$  and  $B$ :

$$A = A_0 e^{i\omega t} + [A_1] e^{i(\omega t - \varphi)}, \quad B = B_0 e^{i\omega t} + [B_1] e^{i(\omega t - \varphi)}$$

$$A = [A_0] \cos(\omega t - \varphi), \quad B = [B_1] \cos(\omega t - \varphi)$$

The time average of the product of the two quantities is then

$$\frac{1}{2} [A_0][B_1] \cos(\varphi - \varphi)$$

This result can be obtained most simply from the complex representation as

$$\frac{1}{2} \text{real Part of } (A^* B) \quad (16-7)$$

## 16. HIGH-FREQUENCY RESISTANCE

Having calculated  $\frac{1}{2} c [\mathbf{E} \times \mathbf{H}^*]$  for the normal conductor, we obtain its value for the superconductor by substituting  $\mathbf{k}$  for  $\mathbf{k}_n$  and multiplying by the factor 16-4. From the real part of this we derive the Joule heat  $Q$  and the resistance

$$R = \frac{Q}{I^2} \quad (16-8)$$

As the factor 16-4 becomes unity and  $\lambda \rightarrow k_n$  when  $\lambda$  approaches infinity, the resistance of the superconductor goes over continuously into that of the normal conductor at the transition temperature provided that the conductivity  $\sigma$  is not discontinuous there.

The simplest solutions of the differential equations 16-1 and 16-2, corresponding to the plane waves already discussed in Chap. 15, are

$$\mathbf{H} = \mathbf{H}_0 e^{-k_n z}, \quad \text{or}$$

Evidently the real part of  $\mathbf{k}$  or of  $\mathbf{k}_n$ , respectively, determines the decrease of amplitude with increasing  $z$ . Separating the real and imaginary parts of  $\mathbf{k}$  and  $\mathbf{k}_n$ ,

$$\mathbf{k} = \frac{1}{c} \sqrt{\frac{2}{3}} \left[ (1 + \sqrt{1 + (\omega \sigma \lambda)^2})^{1/2} + i(-1 + \sqrt{1 + (\omega \sigma \lambda)^2})^{1/2} \right] \quad (16-9)$$

The real part of  $\mathbf{k}$  is thus greater than that of  $\mathbf{k}_n$ , or waves in the superconductor decay more rapidly toward the interior than they do in the normal conductor; other things being equal, as already observed in section (a).

(c) Using the method described above we calculate the  $a-c$  resistance of a circular cylinder of radius  $R$  carrying a current  $I e^{i\omega t}$ , first for a normal conductor. We use the same cylindrical coordinates as in Chap. 8. As the differential equation 16-2 differs from  $d^2 u/dt^2 - \theta^2 u = 0$  only in the notation used for the constants, we can take over eq. 8-9 for the current by replacing  $\theta$  by  $\mathbf{k}_n$  and I by  $I e^{i\omega t}$ .

$\mathbf{I} = 0, \quad \mathbf{I}_0 = 0, \quad \mathbf{I}_1 = \frac{i k_n J}{2 \pi R} e^{i\omega t} \frac{I_0(i k_n R)}{I_1(i k_n R)} \quad (16-10)$

Taking over eq. 8-11 in the same way satisfies eq. 16-5;

$$\mathbf{H}_0 = 0, \quad \mathbf{H}_1 = \frac{i}{2 \pi R} e^{i\omega t} \frac{I_1(i k_n r)}{I_0(i k_n R)}, \quad \mathbf{H}_n = 0 \quad (16-11)$$

For thin cylinders ( $\mathbf{k}_n R \ll 1$ ) to a first approximation  $I_0(i k_n r) = 1$  and  $I_1(i k_n r) = \frac{1}{2} k_n r$ ; compare the series 8-6. We therefore conclude, as in Chap. 8, that the current is uniformly distributed over the cross section in this case. For thick cylinders ( $\mathbf{k}_n R \gg 1$ ) we have approximately:

$$I_0(i k_n r) = (2 \pi / k_n r)^{-1/2} \left( 1 + \frac{1}{8 k_n^2 r^2} \right)^{-1/2} \exp(k_n r + \frac{1}{4}) \quad (16-12)$$

<sup>2</sup>It is essential here that the real part of  $k_n$  be positive.

It follows that  $I$  and  $H$  decay exponentially with decreasing  $r$ . There is a protective layer of thickness  $(Rk_s k_s)^{-1}$  in this case and the skin effect is pronounced.

The Poynting energy flow vector has only one component, an  $r$  component with magnitude  $c E_r H_\theta = -c(a) I_\theta H_\theta$ . The mean rate at which energy enters unit length of the cylinder is therefore

$$Q = 2\pi R \frac{c}{2\sigma} \operatorname{Re} [I_\theta H_\theta] r^{-k}$$

Let  $Z$  be defined in such a way that

$$Q = I^2 \operatorname{Re} (Z)$$

$$(16-11)$$

$$(16-12)$$

so that by eq. 16-5 the resistance per unit length is

$$W = \operatorname{Re} (Z)$$

$$(16-13)$$

$$(16-14)$$

$$(16-15)$$

$$(16-16)$$

$$(16-17)$$

$$(16-18)$$

$$(16-19)$$

$$(16-20)$$

$$(16-21)$$

$$(16-22)$$

$$(16-23)$$

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$$(16-25)$$

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$$(16-30)$$

$$(16-31)$$

$$(16-32)$$

$$(16-33)$$

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$$(16-62)$$

$$(16-63)$$

The resistance turns out to be proportional to  $(\omega \sigma)^{1/2}$ , because the number  $\omega \sigma \lambda$  is a measure of the extent to which the ohmic current  $i$  participates in the transport of electricity, whereas the Joule heat is proportional to the square of  $|i|$ . In the denominator of eq. 16-18 there is the product of the cylinder's circumference,  $2\pi R$ , and the penetration depth  $c/\lambda$ , and this is an approximate measure of the area that carries the current. Multiplying this is the conductivity  $\sigma$ , because it is this product of cross-sectional area and conductivity that matters. We may take  $c/\lambda$  rather than the reciprocal of the real part of  $k$  to be the penetration depth because the supercurrent far outweighs the ohmic current in the present approximation.

Equation 16-18 can be used for all temperatures that are at least some tenths of a degree below the transition temperature, for  $\lambda$  then has assumed order of magnitude,  $10^{-41}$  sec. With increasing temperature  $\lambda$  increases and so does the resistance. However, some tenths of a degree above the transition temperature,  $\lambda$  becomes so great that the equation fails. To discuss the temperature dependency of the resistance in general we introduce the auxiliary quantity  $\theta$  defined by

$$\omega \sigma \lambda = \tan \theta \quad 0 < \theta \leq \frac{1}{2}\pi \quad (16-19)$$

Neglecting the small second term inside the bracket in eq. 16-16 we get the transformation

$$2\pi c R Z = i \omega / \sqrt{\lambda \cos \theta} e^{-i\theta} \quad (16-20)$$

The real part of this is therefore

$$2\pi c R W = \sqrt{\frac{\omega}{\sigma}} | \omega \sigma \lambda \cos \theta \sin \frac{1}{2}\theta = \sqrt{\frac{\omega}{\sigma}} | \sin \theta \sin \frac{1}{2}\theta | \quad (16-21)$$

At the transition temperature,  $\lambda \rightarrow 0$  and therefore  $\theta = \lambda/\pi$ . As the conductivity has perhaps a different value at the transition temperature than at lower temperatures, we have to put

$$2\pi c R W_e = \sqrt{\frac{\omega}{\sigma_e}} \quad (16-22)$$

Dividing eq. 16-20 into the previous equation yields

$$\text{From the way it was derived, eq. 16-20 evidently gives the resistance of a normal conductor having conductivity } \sigma_e \text{ assuming a pronounced skin effect: } \operatorname{Re} (R_e k_e) \gg 1. \text{ This is easily confirmed from eqs. 16-3 and 16-15. Therefore eq. 16-21 again shows that there is a continuous transition from the high-frequency resistance of the normal conductor to that of the superconductor.}$$

(e) All quantities depending on the geometry of the superconductor have disappeared from eq. 16-21, and in fact this equation holds for other forms than the straight circular cylinder.

To see this let us consider a normal conductor having some elongated part. It could, for example, be a wire wound in the form of a coil. At a distance  $L$  from the ends of which the current leads are attached, at a distance  $L$ , resistance would be  $L/A$ , where  $A$  is the mean cross section. However for alternating current with pronounced skin effect, the current does not fill the whole cross section, but only a thin superficial layer the thickness of which is given by  $(Re k_s)^{-1}$ . Let the cross section of this surface layer become a mean linear dimension  $S$  normal to its thickness. Then the resistance becomes  $W = L/(Re k_s)/S$ .

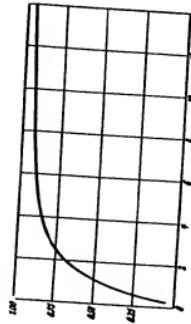


Fig. 16-1. Curve of  $\frac{1}{2} \sin \frac{1}{2} \theta$  against  $\tan \frac{1}{2} \theta$ .

As the example of the cylinder shows, the calculation leads initially to a complex quantity  $Z$  the real part of which is the resistance  $W$ . The equation for  $Z$  can be nothing else than  $Z = L/\omega_0 S$  because the real and imaginary parts of  $k$  do not appear explicitly. In fact the eq. 16-13 does have this form if we remember that it refers to  $L = 1$ , and if, in accordance with eq. 16-15 we put the ratio of the Bessel functions equal to  $-i$ . Going over to the superconductor, which requires the replacement of  $k_s$  by  $k$  and the multiplication by the factor 16-4 we obtain

$$Z = \frac{Lk}{S} \frac{\omega}{\sigma} \frac{(1 + i\omega k)}{(1 - i\omega k)}$$

By again applying eq 16-15 we confirm that the factor  $(L/S)$  equals the factor  $(1/2)R$  in eq. 16-14. This means, however, that the transformation that followed eq. 16-19 can be applied exactly to the expressions  $S/Z/L$  and  $S/W/L$ , thus again leading to eq. 16-21. We repeat: In all these examples it is important that the skin effect should already be pronounced to eq. 16-13 needed for a normally conducting wire wound in the form of a coil. Pronounced skin effect, it consists of a  $\pi$  factor depending only on the spacing between successive windings of the coil and the radius of the wire. The same factor has to multiply  $W = Re Z$ ; it can be taken over unchanged for the superconducting wire and so cancels in eq. 16-21 when forming the ratio  $W/H$ .

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in the normal conductor. It is only if the smallest possible value of  $|k_s|$ , namely  $|k_s|_c$ , satisfies the condition  $|k_s|/R \gg 1$  that eq. 16-21 can be used for the cylinder.

(1) Let us reduce the temperature  $T$  starting from the transition temperature  $T_c$ . According to eq. 16-19  $\theta$  then decreases monotonically with  $\lambda$ , and the same is true of the function  $\frac{1}{2} \sin \frac{1}{2} \theta \sin \frac{1}{2} \theta$  (Fig. 16-1). If finally the number  $\omega \sigma \lambda$  becomes small compared with unity, owing to the decrease of  $\lambda$ , then also  $\theta \ll 1$  and  $\frac{1}{2} \sin \frac{1}{2} \theta \sin \frac{1}{2} \theta$  has the value  $\frac{1}{2} \sin \frac{1}{2} \theta$ . Therefore, according to eq. 16-21, we have

$$W = W_0 \sqrt{\frac{\sigma_0}{2\omega_0}} \omega^2 \sigma^2 \lambda^2$$

in agreement with eq. 16-17.  $W$  should decrease monotonically between this value and  $W_0$ , provided the conductivity  $\sigma$  remains constant. However, the curves published by McLean and co-workers [Chap. 1 (6)] for the resistance of tantalum as a function of temperature for frequency  $\omega = 2\pi 1.14 \times 10^7$  per sec. i. e., the upper curve of Fig. 16-2 shows an initial maximum at which  $W$  is 4% higher than  $W_0$ , and only after this does the expected decrease appear. If this maximum is real, it can only be interpreted as due to the conductivity of starting to decrease at the transition temperature; according to eq. 16-21 the product  $\sqrt{\omega \sigma}$  must decrease immediately below the transition temperature.

It is evidently impossible to determine both  $\sigma$  and  $\lambda$  as functions of  $T$  from a single empirical curve. But by using the empirical curve for  $W$  we can try to find a plausible form for  $\sigma$  as a function of  $T$  such that one derives a curve for  $\lambda$  that has a steep decline just below  $T_c$ , similar to that found in the experiments of Appleyard and Shoenberg with mercury [Chap. 1 (e)]. If  $W$  and  $\sigma$  are given for a certain  $T$ , then eq. 16-21 ascribes to this  $T$  a certain  $\lambda$  value, and eq. 16-19 a certain  $\lambda$  to this  $\theta$ . We try the form

$$\frac{\sigma}{\sigma_0} = 0.6 + 0.4 \times e^{-\alpha(T-T_c)}$$

Fig. 16-2. Resistance of tantalum near the transition temperature.

<sup>1</sup>Precise work on resonant cavities instead of wires failed to show this maximum.

J. C. Slater, R. Maxwell, P. Marcus, *Phys. Rev.* 78, 1532 (1949);  
B. Pippard, *Proc. Roy. Soc. (London)*, 191, 370, 385, 399 (1947); 206, 195, 210, (1950).

according to which  $\sigma$  decreases to 0.6 or within one degree and then remains constant. The empirical values of  $\sigma$ , differ. The finding of McLellan and his co-workers<sup>1</sup> that the d-c resistance of tantalum at  $T_c$  is 0.07% of the resistance at  $0^\circ\text{C}$  leads to  $\sigma_1 = 1.30 \times 10^{13}$  per sec in Lorentz units, and if it is wrong by a factor  $a$ , then all  $\sigma$  values have to be multiplied by  $a$  and all  $\lambda$  values by  $1/a$ , which does not change the form of the  $\lambda$  curve. The result of this calculation is shown in Fig. 16-3. The curve has indeed the expected form. Figure 11-3 gives the measurements of  $\lambda$  for mercury for comparison.

If this is considered a sufficient confirmation of the theory, we can proceed to ask how the  $W$  curve would be affected by going to higher frequencies. We see that the curve must be considerably raised by this at the lowest temperatures where  $W$  is still just noticeable, because of the factor  $\omega_1$  in eq. 16-18. It must also be at higher temperatures because according to eq. 16-19  $\theta$  increases with  $\omega_1$ , and so therefore does the righthand side of eq. 16-21 at a given temperature ( $\theta$  and  $\lambda$  fixed). However, this increase is less serious than the factor  $T$  approaches  $T_c$ . As we already saw,  $\theta$  has its greatest possible value  $\pi/2$  for all frequencies at  $T_c$  itself, so that  $W$  remains equal to  $W_c$  there. The rate of the  $W$  curve up to  $W_c$  becomes less steep with higher frequencies, and the curve should rise appreciably above the zero level at lower temperatures as shown in Fig. 16-2.

(f) H. London measured the resistance of superconducting tin at frequencies of about 10<sup>10</sup> cycles per second by producing eddy currents in an ellipsoidal specimen and calculating the heat produced by measuring the rate of evaporation of the helium bath. He also found that the high frequency resistance of the normal conductor passes continuously into that of the superconductor at the transition temperature, and that there is then a steep drop when we further decrease the temperature.

The considerations of this chapter become meaningless — as does the Maxwell theory itself — if the mean free path of the electrons becomes

comparable with or greater than the penetration depth. Deviations of this kind were first observed by Pippard<sup>2</sup> and by Slater and co-workers.<sup>3</sup> A theoretical treatment of this problem has been given by Reuter and Sondheimer<sup>4</sup> and Slater et al.<sup>5</sup>

### CHAPTER 17

#### Thermodynamics of the Transition between Normal and Superconducting Phases

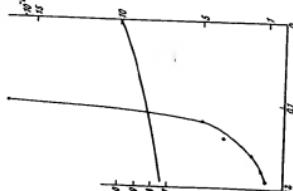
(a) It was the Meissner effect that led to the idea that the superconducting and the normally conducting states are different phases of the same material in the sense that diamond and graphite are different phases of carbon. Earlier, when it was supposed that any arbitrary magnetic field could be "frozen in" within the interior of a superconductor (see Chap. 1) one had to presume an infinity of different superconducting states, and this excluded the phase idea. We know now, however, that the interior of a sufficiently thick superconductor in a stationary state is field free, protected by the thin surface layer, regardless of its history. Even if the metal is too thin to form this protective layer, the field in its interior is uniquely determined by the conditions imposed by the magnetic field in its neighborhood at the moment of interest, and independent of its previous history, always supposing this field to be stationary and changes of state as quasistationary just as we do in all thermodynamic arguments.

However, the superconducting and normally conducting phases are much more alike than diamond and graphite. At all temperatures they have the same lattice structure, not only with regard to symmetry characteristics, but also the same lattice constants. Shape and volume are completely preserved during the transition. This point is essential to the following application of thermodynamics. It would not be if the transition between the two phases were effected by means of an intermediate vapor phase, a certain amount of one phase evaporating, the same amount condensing into the other solid phase. But in the present case one solid phase changes directly into the other, which is in contact with it; only the identity of the two lattices prevents the system from splitting into more or less minute fractions (being of the form single crystal  $\rightarrow$  polycrystal which would naturally exclude any reversibility).

<sup>2</sup> D. Pippard, *Proc. Roy. Soc. (London)*, 191, 370, 385, 399 (1947).

<sup>3</sup> J. C. Slater, E. Maxwell, P. Marcus, *Phys. Rev.*, 76, 1332, (1949).

<sup>4</sup> G. E. H. Reuter and E. H. Sondheimer, *Proc. Roy. Soc. (London)*, 195 A, 336 (1948).



Incidentally Keesom and Kool<sup>1</sup> (for rubidium) and van Laer and Keesom<sup>2</sup> (for tin) have experimentally compared the heats of reaction during the transition both from the superconductor to the normal state and during the reverse transition and have found them equal, as required for reversibility.

A further assumption, supported indeed by the arguments of Chap. 5, is that the free energy of the magnetic field, including the superconducting energy is added to the free energy of the specimen, and so there is no free "machine" exerting the forces on the superconductor. The field is a force given by the London stress system as discussed in Chap. 13. These forces perform work in so far as the surface is displaced, and this work serves to change the free energy of the material during isothermal displacements. The free energy of the field does not enter such a calculation, the internal changes of the "machine" being irrelevant for the energy balance in the specimen.

As shown in Chaps. 13 and 14 the force due to the field at a point where no current crosses the surface — the current lines being parallel to the surface — is a stress of amount  $\frac{1}{2}(\mathbf{H} \cdot \mathbf{G})$  directed toward the interior of the superconductor. We shall discuss this example first.

(b) To do this we write  $f_s$  and  $f_n$  for the free energies ( $f = -T\delta$ ) for the mol of the superconductor and normal conductor respectively and  $V$  for the mol volume common to both phases, with  $d\mathbf{a}$  a surface element in the direction of its normal.  $d\mathbf{a}$  is taken positive for displacements toward the interior of the superconductor as in Chap. 14 (f). It is necessarily positive whenever the superconductor borders upon empty space or a chemically different specimen, but  $d\mathbf{a}$  can be negative if the superconductor joins on to a chemically identical normal conductor. For positive  $d\mathbf{a}$ ,  $d\mathbf{n} \cdot d\mathbf{a}/V$  of the London stress change into normal conductor; the tension while the free energy of the material increases by  $(f_n - f_s) d\mathbf{a} \cdot d\mathbf{n}/V$ . For negative  $d\mathbf{a}$  the corresponding number of mol of normal conductor change into superconductor; the work done by the forces becomes negative. Naturally it is impossible for a single element alone to be displaced as the continuity of the boundary must be preserved, but an arbitrary infinitesimal displacement  $d\mathbf{n}$  can be ascribed to any element  $d\mathbf{a}$  of the surface. The total number of mol going over from one phase into the other is  $\int d\mathbf{n} \cdot d\mathbf{a}/V$  and the work done by the forces is

$$\delta A = \frac{1}{2}(\mathbf{H} \cdot \mathbf{G}) d\mathbf{n} \cdot d\mathbf{a}$$

The corresponding change in free energy is

$$W = W_H - W_{H_0} = \frac{1}{2} H^2 V$$

<sup>1</sup>W. H. Keesom and J. A. Kok, *Physica*, 1, 503 (1934).

<sup>2</sup>P. H. van Laer and W. H. Keesom, *Physica*, 5, 995 (1938).

$$\delta F = \left[ \frac{(f_n - f_s)}{V} \right] \int d\mathbf{n} \cdot d\mathbf{a} \quad (17-2)$$

From the two principal laws of thermodynamics one concludes that for a spontaneous isothermal transition  $\delta A > \delta F$ . The necessary condition that a transition shall not occur is therefore

$$\delta A \leq \delta F$$

Applied to the displacement of the boundary this gives

$$\frac{1}{2} \int (\mathbf{H} \cdot \mathbf{G}) d\mathbf{n} \cdot d\mathbf{a} \leq \left[ \frac{(f_n - f_s)}{V} \right] \int d\mathbf{n} \cdot d\mathbf{a}$$

Since  $d\mathbf{n}$  can be either positive or negative, the inequality must reduce to equality: because if for some choice of  $d\mathbf{n}$  on the right-hand side were greater than the left side, it would be smaller for the opposite choice of  $d\mathbf{n}$ . Furthermore, as  $d\mathbf{n}$  is an arbitrary function of position on the surface, equilibrium must exist at every point:

$$\frac{1}{2} (\mathbf{H} \cdot \mathbf{G}) = \frac{(f_n - f_s)}{V} \quad (17-5)$$

This is the equilibrium condition for the boundary between super- and normal conductor. If  $d\mathbf{n}$  is necessarily positive at the surface of a superconductor bordering empty space or a chemically different specimen the condition for conservation of superconductivity is

$$\frac{1}{2} (\mathbf{H} \cdot \mathbf{G}) \leq \frac{(f_n - f_s)}{V} \quad (17-6)$$

In this form both conditions are valid for "thick" superconductors with fully developed protective layers, as well as for the "thin" superconductors in which the magnetic field penetrates more or less completely. Since experiments almost always deal with "thick" superconductors these conditions are usually expressed instead in terms of the magnetic field at the surface, derived from the supercurrent there by the eq. 1-37 valid for "thick" superconductors. We define a field strength  $H_z$  by

$$\frac{1}{2} H_z^2 = \frac{(f_n - f_s)}{V} \quad (17-7)$$

The condition 17-3 for the boundary between super- and normal conductor reads

$$H = H_z \quad (17-6)$$

and the condition 17-4 for a boundary surface adjacent to empty space or a chemically different material:

$$H \leq H_z \quad (17-7)$$

This justifies our considering  $H_z$  defined by eq. 17-5 as a critical field. It is a necessary consequence of this theory that if  $H$  exceeds this value at any point of the free surface of a "thick" superconductor its superconductivity is destroyed.

If the magnetic field gives rise only to permanent magnetism and angular currents in superconductors, then according to Chap. 14 (e) the work performed by the field is equal to the decrease  $(-\delta U)$  of the free energy of the field. Equation 17-3 states that in this case the sum of the free energy of the field and the specimen is conserved during the reversible phase transition. This statement however does not hold if ohmic currents are also produced, or if only ohmic currents are produced by the field. In this case the system (field plus specimen) is not a closed system. Additional electrostatic forces are required to fulfill the condition that the ohmic currents remain constant.

If we wish to use the theorem of constant free energy we have to be quite clear about how the field is produced. (c) These conclusions can also be derived for a "thick" superconductor from the volume forces exerted according to Chap. 15 by the Maxwell stresses,  $[1 \times H]/c$ , on the supercurrent mechanism of the London theory. These forces are distributed over the thickness of the protecting layer. However, in the "thick" superconductor this protecting layer undergoes a virtual displacement  $\delta n$  as a whole without alteration of field or current distribution, so that we can calculate the work done by these forces per unit surface as the product of the resultant force per unit area times  $\delta n$ . As there is no field inside the layer, the resultant force is the pressure  $1/2 H^2$  of the lines of force on the outside, by Chap. 15. In this way we get the equilibrium condition

$$\delta A = \frac{1}{2} \int \mathbf{H}^2 d\mathbf{n} \cdot d\mathbf{s} \leq \left[ \frac{(n - s)}{V} \right] \int d\mathbf{n} \cdot d\mathbf{o}$$

and from this, the eqs. 17-6 and 17-7. This conclusion cannot be assumed so easily for thin superconductors where the field and current distribution change in a complicated fashion with a displacement  $\delta n$  of the surface. This derivation has the advantage of being based more directly on the Meissner effect, i. e., the existence of the protective layer, than was the first derivation; but the latter is more general and can be used also for thin specimens.

(d) The free energies  $N$  and  $S$  are functions of the temperature  $T$ . We neglect their dependence on pressure or elastic stress because most experiments have been performed on strain-free specimens at one atmosphere which is effectively zero pressure. According to eq. 17-5 the critical value  $H_c$  is also a function of  $T$ . From thermodynamics we have<sup>a</sup>

$$S = -\frac{dI}{dT} \quad (17-8)$$

for the entropy per mol,  $s$ , and we obtain eq. 17-5 by neglecting the extremely small changes in volume  $\delta V$  at these temperatures in accordance with Nernst's theorem, thus:

$$S - S_0 = -\frac{1}{2} V \frac{d(H_c^2)}{dT} = -V H_c \frac{dH_c}{dT} \quad (17-9)$$

The specific heat does not depend on magnetic field (see discussion of Fig. 17-2) so we may write  $dI/dT$  instead of  $(\partial I/\partial T)_{H_c}$ .

This is the increase in entropy associated with the transfer of one mol from the superconducting to the normal state. Multiplying by  $T$  we get the amount of heat that has to be supplied with this transition:

$$Q = -\frac{1}{2} V T \frac{d(H_c^2)}{dT} = -V' T H_c \frac{dH_c}{dT} \quad (17-10)$$

Further we have the following expression for the specific heat per mol at constant pressure:

$$c = T \frac{ds}{dT} = -T \frac{d^2}{dT^2} \quad (17-11)$$

So from eq. 17-9 we have

$$c_V - c_S = -\frac{1}{2} V T \frac{d^2(H_c^2)}{dT^2} = -V' T \left[ \frac{(dH_c)^2}{dT^2} + H_c \frac{d^2H_c}{dT^2} \right] \quad (17-12)$$

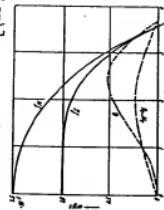


Fig. 17-1. Thermodynamic functions for tin below the transition temperature  $N$  and  $S$  are the free energies per mol in the normal and superconducting states. The curves split at the transition temperature 3.7° K. Only the difference  $N - S$  has physical meaning. The upper dotted curve gives the heat  $Q$  in ergs per mol to be supplied during the transition of the superconductor into the normally conducting state. The lower dotted curve is the entropy difference  $S_V - S_S$  in ergs per mol degree. The figures used come from eqs. 17-16 and 17-17.  
 $N = 2.64 \times 10^{-7} T^4 - 8.40 \times 10^4 T^3 + 1.50 \times 10^8 \text{ erg/mol}$   
 $S = 5.92 \times 10^{-7} T^4 + 1.00 \times 10^4 \text{ erg/mol deg}$   
 $Q = 1.35 \times 10^{-7} T^4 + 1.68 \times 10^4 \text{ erg/mol}$

(e) These relations were first derived by Rutgers<sup>4</sup> and by Casimir and Gorter.<sup>5</sup> We shall discuss them now in the light of the free energy curves,  $N$  and  $S$  as functions of  $T$ , represented in Fig. 17-1. The slopes, or tangents

<sup>4</sup>A. J. Rutgers, *Proc. Roy. Acad. (Amsterdam)*, 36, 185 (1933).

<sup>5</sup>H. B. G. Casimir and C. J. Gorter, *Physica*, 1, 300 (1934).

<sup>6</sup>A formulation also valid for superconductors was given by Max von Laue, see Chap. I, footnote 7, and Chap. 5, footnote 2 (f).

give the corresponding entropy, by eq. 17-8.  $H_c$  is zero at the transition temperature  $T_c$ , by definition, therefore  $f_c = f_s$  there according to eq. 17-8, and the two curves coincide. Experiment shows that  $dH/dT$  is finite at  $T_c$ , so that by eq. 17-9 the two curves have a common tangent. But by eq. 17-12 the curves differ in their second derivatives, i. e., curvature. For  $T < T_c$  we always have  $f_c > f_s$  according to eq. 17-5.

We cannot produce the curve of  $f_s$  above  $T_c$  because the superconductor does not exist there, not even as a phase that is unstable with respect to the normal conductor. We arrive at this conclusion first from the fact that the supercurrent constant becomes infinite at  $T_c$ , so that no value can be ascribed to it above  $T_c$ . Secondly, from the fact that when  $f_s - f_c$  is developed in a power series in  $T - T_c$ , it must start at the value  $f_s - f_c$  so that the common point of the two curves would be a stationary point,  $f_s$  would then be greater than  $f_c$  above  $T_c$ , which is inconsistent with the whole concept of phase transitions. Approaching the transition from above, the free energy curve divides at  $T_c$  in such a way that the two branches originating at  $T_c$  have the same initial tangent.

Experience shows that  $H_c$  increases monotonically with decreasing temperature. According to eq. 17-5 the same must be true of  $f_s - f_c$ . At  $T = 0$ ,  $f_s - f_c$  must vanish by the Nernst theorem. Therefore by eq. 17-9 it follows that  $(d^2H_c/dT^2)_{T=0} = 0$ . The parabola drawn in Fig. 1-4 satisfies this condition and also the condition that  $dH/dT$  remains finite at  $T_c$ , without however being fixed by these conditions. On the other hand  $dH_c/dT < 0$  and therefore by eq. 17-10  $\dot{Q} > 0$ : *The transition from the superconducting to the normally conducting state requires heat: the former process liberates heat.*

$\dot{Q} = 0$  only at the absolute zero where also the factor  $dH/dT$  in eq. 17-9 vanishes as well as  $T$ , and at the transition temperature  $T_c$  where the factor  $H_c$  vanishes. Between these temperatures  $\dot{Q}$  has at least one maximum. If the  $H_c$ -temperature curve is exactly parabolic as in Fig. 1-4 the only maximum is at  $T = T_c/\sqrt{2} = 0.707 T_c$ . From the finite value of  $dH_c/dT$  at  $T_c$  we conclude by eq. 17-10 that  $dH_c/dT < 0$  and  $d^2H_c/dT^2 < 0$  in the neighborhood of the absolute zero where  $d^2H_c/dT^2$  is still small,  $f_s - f_c$  must be positive if  $\dot{Q}$  is an intersection of the curves of  $f_s$  and  $f_c$  as functions of  $T$ . In between there must be an intersection of  $f_s$  and  $f_c$  as functions of  $T$ . The entropy difference  $s_s - s_c$  has a maximum at this point, by eq. 17-11. If the  $H_c - T$  curve were exactly parabolic, this intersection would occur at  $T = T_c/\sqrt{3} = 0.575 T_c$ . At  $T = 0$  both  $f_s$  and  $f_c$  are zero by the Nernst theorem.

In these calculations current density  $I$  and field strength  $H$  were expressed in Lorentz units. Transforming to electrostatic units  $H_s$  has to be multiplied by the factor  $1/4 \pi$ , according to eq. 3-10. Equations 17-5, 17-10, and 17-12 expressed in electrostatic units read:

$$\frac{V H_s^2}{8\pi} = f_s - f_c \quad (17-13)$$

$$Q = \left( \frac{V}{8\pi} \right)^2 \frac{dH}{dT} \quad (17-14)$$

$$c_V - c_S = - \frac{V}{8\pi} T^2 \frac{d^2H}{dT^2} \quad (17-15)$$

According to eqs. 3-10 and 3-11 the general conditions 17-3 and 17-4 retain their form in the electrostatic system.

We are now in a position to derive from eq. 17-12 an equation that has often been used to check the theory against experimental evidence. By partial integration we have

$$-\int (c_V - c_S) dT = \frac{1}{2} V \int_T^{T_c} \frac{d^2H/dT^2}{dT^2} dT = \frac{1}{2} \left[ \left| \frac{d(H/f)}{dT} \right|_T^{T_c} - \int_T^{T_c} \frac{d(H/f)}{dT} dT \right] \quad (17-16)$$

At  $T_c$ ,  $H_c = 0$  and  $d(H/f)/dT = 0$ . Using these expressions and eq. 17-10 to transform the right-hand side we obtain

$$-Q = \frac{1}{2} V H_c \int_T^{T_c} \frac{d^2f}{dT^2} dT \quad (17-16)$$

This equation expresses the energy principle for the following cycle: Consider one mol of substance:

1. Cool the superconducting phase from the transition temperature  $T_c$  to  $T$ . To effect this we have to supply the (negative) amount of heat

$T$  to  $T_c$ , for which we have to supply heat amounting to  $\int_{T_c}^T c_V dT$ .

2. Transform the superconducting phase into the normally conducting phase isothermally by application of the magnetic field  $H_c$ ; this requires the supply of heat  $Q$  and the performance of work  $\frac{1}{2} V H_c^2$  (see Chaps. 13 and 14).

3. Heat the normally conducting phase in the magnetic field  $H_c$  from  $T_c$  to  $T$ , for which we have to supply heat amounting to  $\int_{T_c}^T c_V dT$ .

4. Remove the magnetic field and transform the material at  $T_c$  into the superconducting state. This step requires no heat and no work. By equating the sum of all these amounts of heat and work to zero we obtain eq. 17-13.

If Fig. 1-4 is correct,  $H_c$  for lead increases to almost 1000 oersteds. eq. 17-13, the quotient of the mass of one mol, 207 g., and the density,  $11.3 \text{ g. cm.}^{-3}$ , is about 18 cm.<sup>3</sup> Therefore  $10^5 \text{ erg} = 7.5 \times 10^5 \text{ g. cm.}^{-3}$ .

For comparison we may mention that the difference of free energies

of water and ice per mol is about  $1.6 \times 10^6 \text{ erg}$  at  $0^\circ \text{C}$  and approximately

$10^4$  dynes/cm<sup>2</sup> pressure; and  $4.6 \times 10^8$  erg at  $-20^\circ\text{C}$  and about  $1.9 \times 10^8$  dynes/cm<sup>2</sup>.

In the neighborhood of the transition temperature, where  $H_c$  is smaller by one or two powers of 10,  $\kappa_s - \kappa$  is smaller by two to four powers of 10, and therefore quite small compared with the above values for water and ice.

Using the equation for the transition curve from which Fig. 1-4<sup>a</sup> was drawn,

$$H_c = a(T_c^4 - T^4), \quad a = 17.3 \text{ oersted/deg}^4, \quad T_c = 7.3^\circ\text{K}$$

Calculating the maximum of the heat of transition at  $6.2^\circ\text{K}$  and the difference between the specific heats at the transition temperature, we find:

$$Q_{\text{max}} = 6.2 \times 10^4 \text{ erg} = 1.5 \times 10^{-3} \text{ cal (Baud)}$$

and

$$(c_V - c_S)_T = 6.9 \times 10^4 \text{ erg/deg} = 1.6 \times 10^{-3} \text{ cal/deg (Baud)}$$

These figures at least give some idea of the magnitude of the values under discussion.

(f) The Rutgers-Gorter-Casimir equations 17-6, 17-9, 17-10, and 17-12 have been confirmed for several metals. We may mention here the measurements on Zn by Keston and van Laer,<sup>6</sup> and in Fig. 17-2 the points C shown the experimental results for the molar heat found in the absence of a magnetic field. Starting above the transition temperature  $T_c$ , these points of  $3.7^\circ\text{K}$ . The points suddenly jump to higher values and trace the curve for  $c_V$  and the points ● in a field of 139 oersteds. As these fields prevented the appearance of superconductivity, all these points lie on the curve for  $c_W$  which apparently does not depend on the field strength. This is an important confirmation of our assumption that the thermodynamic functions of the normal conductor are uninfluenced by a magnetic field. Although  $c_S$  lies much higher than  $c_V$  at the transition temperature, the two curves intersect each other at  $1.9^\circ\text{K}$  as required in section (g).

The authors were able to represent the  $c_V$  curve by Debye's law for

$$c_V = 464.5 \left( \frac{T}{\theta_V} \right)^3 \text{ cal deg}^{-1}, \quad \theta_V = 140^\circ\text{K} \quad (17-17)$$

However, in order to obtain a good representation of  $c_V$  they had to add to the  $T^3$  term a linear term in  $T$ :

$$c_V = 464.5 \left( \frac{T}{\theta_V} \right)^3 + 4 \times 10^{-1} T \text{ cal deg}^{-1}, \quad \theta_V = 185^\circ\text{K} \quad (17-18)$$

In fact, even with this additional term there are still discrepancies above  $3.6^\circ\text{K}$ . The second term may be interpreted as the specific heat of the conduction electrons on the Sommerfeld theory of metallic conductivity.

<sup>a</sup> Calculated as the product of pressure and change of volume. W. H. Keston and W. H. van Laer, *Physica*, 5, 193 (1939). The value  $\theta_c = 140^\circ\text{K}$  was taken from their Fig. 2.

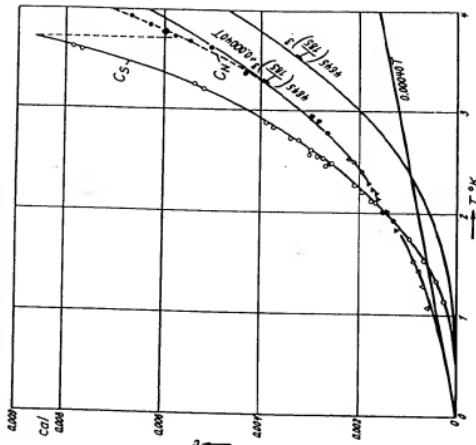


Fig. 17-2. Atomic heat of normal and superconducting tin as a function of temperature.

The jump in the atomic heat of tin at  $T_c$  is  $1.26 \times 10^5 \text{ erg/deg} = 3.0 \times 10^{-2} \text{ cal/deg}$ , according to Fig. 17-2, and so considerably smaller than that found in lead [section (e)]. In addition to the  $c_V$  and  $c_S$  curves in Fig. 17-1 we have also plotted the entropy difference, using the values from eqs. 17-17 and 17-18.

<sup>b</sup> W. J. de Haas and Miss A. D. Engelker, *Physica*, 4, 325 (1937).

$$-(s_y - s_z) = \int_{\Gamma} \frac{1}{r} (c_5 - c_6) dt \quad (17-19)$$

and also the heat of the transformation  $\mathcal{Q} = T(s_y - s_z)$ .

Keesom and van Laer examined the validity of eq. 17-3 by measuring the heat of transformation  $\mathcal{Q}$  and the specific heats of tin. They find agreement between calculated and measured values of  $\mathcal{Q}$  to within 5% in the least favorable case. The confirmation of eq. 17-19 in the same paper shows that the assumption of a reversible phase transition is justified.

(f) A homogeneous magnetic field does not generally need to have the full strength  $H_c$  in order to quench the superconductivity of any body placed in it. As shown in Chaps. 9 to 11 for many examples, and depicted in Fig. 1-5, the distortion of the field by the superconductor produces an intensification of the field at the surface of that body. This suffices for the quenching of the superconductivity if the intensification raises the field at some point to beyond  $H_c$ . If we write for the ratio of the maximum field strength at the surface to the field strength at a great distance from the specimen, the critical value of this latter field is  $H_s/H_c$ . In the sequel we must distinguish carefully between this value, depending on the form of the specimen, and the critical  $H_s$  that depends only on the material of the specimen and the temperature.

For a "thick" elliptical cylinder with axes  $a$  and  $b$ , the  $\hat{\alpha}$  axis forming the angle  $\theta$  with the direction of the field we have, by eq. 10-24:

$$a = \left(1 + \frac{1}{b}\right) \sqrt{a^2 \sin^2 \theta + b^2 \cos^2 \theta} \quad (17-20)$$

The intensification factor  $a$  therefore varies with  $\theta$  between  $1 + b/a$  and  $1 + a/b$ . This has been confirmed at least qualitatively by de Haas and Casimir-Jonker [Chap. 1 (1)]. For the thick circular cylinder  $a = 2$ , for the "thick" sphere  $a = 3/2$ , see Chap. 11.

general equations 17-3 and 17-4. These equations, remembering eq. 17-5, can be written:

$$\langle \hat{\nu} \cdot \hat{G} \rangle = H_s^2 \quad (18-1)$$

$$\langle \hat{\nu} \cdot \hat{G} \rangle \leq H_s^2, \quad (18-2)$$

condition for preserving superconductivity at a free surface

In what follows we discuss cubic superconductors with  $\langle \hat{\nu} \cdot \hat{G} \rangle = \lambda^{-1} \mu^2$ . However, the results are qualitatively valid for other forms.

Consider two geometrically similar thin superconductors of the same material and at the same temperature such that the linear dimensions of the smaller specimen can be obtained from those of the larger one by multiplication by the factor  $a < 1$ . Let the two specimens be placed in the same homogeneous magnetic field  $H_0$ ; then the ratio of the current densities  $\nu$  in the smaller specimen to that at the corresponding point in the larger specimen is, according to Chap. 7 (f), equal to  $a$ . Since  $\nu$  is proportional to  $H_0^2$  we have to increase  $H_0$  by the factor  $a^{-1}$  to get the same stress  $\lambda/2 \lambda^{-1} a^{-1} = \lambda/2 H_0^{-2}$  at corresponding points on the surface of the smaller specimen. The critical value of  $H_s^2$  needed to quench superconductivity increases by the factor  $a^{-1}$  when the dimensions of the specimen are decreased by the factor  $a$ . The smaller the disturbance of the field caused by a small superconductor, the less it is influenced by the field.

(g) We shall prove this for a few examples. For a plane parallel plate of thickness  $2d$  with field strength  $H_0$  at both sides we have by eq. 7-18

$$2d^2 = (H_0^2)^2 \tanh^2(\beta d) \quad (18-3)$$

According to eq. 18-1 the superconductivity is quenched at the critical value

$$H_s^2 = H_0^2 \coth \beta d \quad (18-4)$$

For a "thick" plate this is approximately

$$H_0^2 = H_s^2 (1 + 2e^{-2\beta d}) \quad (18-5)$$

and for a "thin" one

$$H_0^2 = H_s^2 \left[ \frac{1 + (\beta d)^2/5}{\beta} \right] \quad (18-6)$$

#### CHAPTER 18

### The Critical Magnetic Field for Thin Superconductors

(a) It is only for "thick" superconductors that the field strength  $H_s$  defined in eq. 17-5 is a critical value exceeding which at any point of the free surface would destroy the superconductivity. Equation 7-37 between current density and magnetic field strength at the surface holds only for a fully developed protective layer. For "thin" superconductors in which the protective layer is not fully developed, we have to go back to the more

<sup>18</sup>W. H. Keesom and P. H. van Laer, *Physica*, 3, 371 (1936).

The denominator  $\beta d$  corresponds to the factor  $a$  in the theorem of (a). The current density at the surface of a cylinder of radius  $R$  in a longitudinal field  $H_0$  is, according to eq. 10-2, given by:

$$\lambda(\beta R)^2 = (H_0^2)^2 \left[ -\frac{I_{11}(\beta R)}{I_0(\beta R)} \right]^2$$

The critical value is therefore

$$H_0^2 = H_s^2 \left[ \frac{I_1(\beta R)}{I_1(\beta R)} \right]^2 > H_s^2 \quad (18-7)$$

By using eq. 16-15 for the ratio of the Bessel functions for large values of  $\beta R$  we find

$$H^0 = H_s \left( 1 + \frac{1}{2\beta R} \right) \quad (18-6)$$

For small values of  $\beta R$ , however, the series 8-6 gives

$$H^0 = 2H_s \frac{1 + \frac{1}{8}(\beta R)^2}{\beta R} \quad (18-7)$$

For a cylinder in a transverse field the current density at the surface is, by eq. 10-16, a maximum at  $\theta = \frac{1}{2}\pi$ . At this angle

$$(i/r)^2 s_{\theta\phi} = (H/r)^2 \left[ -\frac{i J_1((\beta R))}{I_0((\beta R))} \right]^2$$

This value is four times the value for longitudinal fields. Therefore we have simply to divide the right-hand sides of eqs. 18-5, 18-6, and 18-7 by 2 to get the corresponding results for the transverse field.

The current density at the surface of a sphere of radius  $R$  has, on the equatorial plane  $\theta = \frac{1}{2}\pi$ . According to eqs. 11-1, 11-9, and 11-5 we have

$$\lambda (i/r)^2 s_{\theta\phi} = (H/r)^2 \left[ \frac{3}{2} \coth \beta R - (\beta R)^{-1} \right]^2$$

A homogeneous field can therefore be increased without destroying the superconductivity only as far as the critical value:

$$H^0 = \frac{3}{2} H_s \left[ \coth \beta R - (\beta R)^{-1} \right] > \frac{2 H_s}{3} \quad (18-8)$$

This means for  $\beta R \gg 1$ , up to

$$H^0 = \frac{2}{3} H_s \left( 1 + \frac{1}{\beta R} \right) \quad (18-9)$$

while with  $\beta R \ll 1$ , up to

$$H^0 = 2H_s \frac{1 + \frac{1}{15}(\beta R)^4}{\beta R} \quad (18-10)$$

The denominator  $\beta R$  in eqs. 18-7 and 18-10 again corresponds to the  $a$  factor in the theorem of section (a). We follow these examples by three paradoxes. At the two boundaries  $\pm \frac{1}{2}d$  of a plane parallel plate of thickness  $2d$  carrying current  $i$  per centimeter, the current density and magnetic field are given by eq. 7-21:

$$|i_s| = \frac{1}{2} i / \coth \beta d, \quad |H_s| = \frac{i}{2c}$$

The critical value of  $i$  that quenches superconductivity is such that  $|i_s|^2 = H_s^2$ . Therefore the critical current and the corresponding field intensity are respectively

$$i^* = 2c H_s \tanh \beta d, \quad |H_s| = H_s \tanh \beta d \quad (18-11)$$

The critical current therefore decreases with decreasing  $\beta d$  finally going to zero; the same is true of the corresponding magnetic field. The mean critical current density, however, namely,

$$\frac{i^*}{2d} = \sqrt{\frac{H_s}{\lambda}} \tanh \frac{\beta d}{\beta d} \quad (18-12)$$

increases to a maximum value  $H_d/\sqrt{\lambda}$ . The current density at the surface of a wire of radius  $R$  carrying current  $i$  is, by eq. 8-9

$$(i/r)^2 s_{\theta\phi} = \frac{\beta I}{2\pi R} \frac{i J_0((\beta R))}{I_1((\beta R))} \quad (18-13)$$

To find the maximum possible supercurrent we must put  $\lambda I r^2 = H_d^2$ . This gives the maximum possible mean current density

$$\frac{i^*}{\pi R^2} = \frac{H_d}{\rho} \sqrt{\frac{2}{\lambda}} \frac{i J_0((\beta R))}{I_1((\beta R))} \quad (18-14)$$

The ratio of the Bessel functions decreases more slowly than  $\beta R$ , the mean current density therefore increases, but more slowly than  $(\beta R)^{-1}$ . In particular for large  $\beta R$  we have

$$\frac{i^*}{\pi R^2} = \frac{2 H_d}{\rho \sqrt{\lambda R}} \left( 1 - \frac{1}{2} \beta R \right) \quad (18-15)$$

and for small  $\beta R$

$$\frac{i^*}{\pi R^2} = \frac{H_d}{\rho \sqrt{\lambda}} \left[ 1 - \frac{1}{8} (\beta R)^4 \right] \quad (18-16)$$

$H_d/\sqrt{\lambda}$  is again the maximum possible current density. The magnetic field produced by this maximum current at the surface of the wire is

$$\frac{i^*}{2\pi c R} = - \frac{H_d}{I_0((\beta R))} \quad (18-17)$$

and is thus smaller than  $H_d$ , and the more so the smaller  $\beta R$ , vanishing with  $\beta R$ . These examples do not actually contradict the theorem of section (d), because in both these cases the superconductor was not put into an already existing field. The field outside would not exist without the current  $i$ .

The above results can easily be demonstrated and generalized. The maximum possible current load is characterized by the fact that the current density attains the value  $H_d/\sqrt{\lambda}$  for which the stress is  $\frac{1}{2} \lambda i^4 = H_d^2$  at one or more points on the surface (in both the above examples actually over the whole surface). The mean current density required for this in a "thick" superconductor is actually very small compared with  $H_d/\sqrt{\lambda}$  because of the extended protected region beneath the protecting layer. However, the mean density for a very thin superconductor is equal to  $H_d/\sqrt{\lambda}$  because the current is uniformly distributed over the whole cross section. It can never increase beyond this value under any circumstances.

because according to Chap. 7 the maximum current density is always at the surface. As the cross section decreases toward zero, the maximum possible current and the magnetic field at the surface produced by this current also decrease toward zero. This is shown by eqs. 18-11 and 18-12 for a wire and eqs. 18-14 and 18-16 for a plate.

(d) The third of the mentioned paradoxes is of a different kind. If the bore of a hollow thick cylindrical superconductor contains a magnetic field

$$\lambda_1 \beta^2 = (H^0)^2 \left[ \frac{H_1(1/\beta R)}{H_0(1/\beta R)} \right]^2$$

To make this equal to  $H_s$ , we must have:

$$H^0 = -H_s \frac{H_0(1/\beta R)}{H_1(1/\beta R)}$$

The factor multiplying  $H^0$  is less than unity and is smaller the smaller  $\beta R$ . Whereas for large  $\beta R$  we have

$$H^0 = H_s \left( 1 - \frac{1}{2\beta R} \right)$$

for indefinitely decreasing values of  $\beta R$  the maximum possible value of  $H^0$  goes to zero according to the equation

$$H^0 = -H_s \beta R \log \beta R$$

This decrease with decreasing  $\beta R$  is again no contradiction to section (a), as we are not considering a "thin" superconductor.<sup>4</sup>

As already mentioned in Chap. 12 (f), it can happen that, upon cooling down a normally conducting ring in a magnetic field, at first only an annular part of the specimen becomes superconducting. Normal conductivity remains within the bore of this ring, and a number of lines of force, or rather constant (Chap. 12)  $B_{\theta}$ , are present there. This flux, or rather remain smaller, the field intensity must increase. We see therefore that the bore cannot become arbitrarily small. The critical value of the field strength decreases with the decreasing dimensions of the bore, so that in any case a state will be reached where any further shrinking of the bore will cause the magnetic field to exceed this critical value.

(e) We now come to the measurements of the critical value for "thin" superconductors. Pontius [Chap. 1 (c)] measured the critical values of a longitudinal field for lead wires at  $42^\circ$ , i. e.,  $3.1^\circ$  below the transition temperature. The radii of the wires were of the order of magnitude  $10^{-4}$  cm

<sup>4</sup>The equations of section (b), (c), and (d) were first given by M. V. Laius in the paper already quoted: *Ann. Phys.*, **89**, 145 (1938). An error is seen in that paper led to a wrong result for the cylinder in a transverse field. The numerical values used in section (e) are also taken from that paper.

to  $10^{-3}$  cm. Figure 18-1 shows his observations compared with a theoretical curve calculated, not from eq. 18-6, but by the somewhat more exact equations<sup>5</sup>

$$\left( \frac{H_1}{H_0} \right)^2 = 1 - \frac{1}{\beta R} + \text{terms in } \frac{1}{(\beta R)^2} \quad (18-19)$$

It has been assumed that  $H_s = 537$  oersteds, and then that  $\beta = 4.78 \times 10^4$  cm<sup>-1</sup> to yield by eq. 6-7 the value for  $A$ :

$$A = 4.8 \times 10^{-4} \text{ sec}^2 \text{ in Lorentz units}$$

or by eq. 6-8 the  $4\pi$  times greater value

$$\lambda = 6.0 \times 10^{-6} \text{ sec}^2 \text{ in esu.}$$

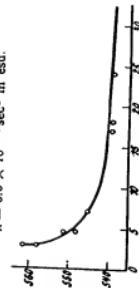


Fig. 18-1. The limiting field strength  $H^0$  in Oersteds as a function of the radius  $R$  of the wire (in  $10^{-4}$  cm units) for lead at  $4.2^\circ$  K. The theoretical curve according to eqs. 18-19 and the points observed by Pontius.

This good agreement between the calculated and observed values not only supports the theory in general, but also supports the orders of magnitude for  $\beta$  and  $A$  proposed by F. London from quantum mechanical considerations. This calculation was made in 1938 and was the first one to be based on observational data.

There are also data for thin films. Shainikov [Chap. 1 (e)] used a lead film  $1.4 \times 10^{-4}$  cm thick and a tin film  $1.1 \times 10^{-4}$  cm thick and found

\*From eq. 8-7

$$-\frac{I_1'(iX)}{I_0(iX)} - \frac{d \log I_0(iX)}{dX}$$

and by eq. 16-10

$$I_1(iX) = \frac{e^X (1+i/X)}{\sqrt{2\pi X}}$$

therefore

$$-\frac{I_1'(iX)}{I_0(iX)} - 1 - \frac{1}{X} + \text{terms in } \frac{1}{X^2}$$

Equation 18-6 should be more exactly  

$$H^0 = H_s \left[ 1 + \frac{1}{2\beta R} + \frac{3}{8(\beta R)^2} \right]$$

that the critical magnetic field strength required to quench superconductivity was far higher than the critical value  $H_c$  found for "thick" films from  $H_c$ , the critical current load was much smaller than that calculated ranging over several degrees. They correspond qualitatively with the results of sections (b) and (e). They agree also qualitatively with those of Applequist and Misener [Chap. 1 (e)] on the critical magnetic field values in mercury films from  $4 \times 10^{-4}$  to  $1 \times 10^{-4}$  cm thick. Shatzikov's results do not seem suitable for a quantitative check of eq. 18-2 or the determination of  $\beta$  because they do not agree quantitatively with the measurements of Applequist, Bristol, and H. London [Chap. 1 (c)] for mercury films of a similar thickness. The last mentioned authors, however, arrived at an estimate of the relative value of  $\beta$  at any  $T$  to its value at 2.56 K. in the same manner. As the critical value depends only on the product  $\beta/\kappa$ , they selected from among their data, at different temperatures and thicknesses those which yielded the same critical value. Then  $\beta/\kappa$  must have the same value for all these cases; thus

$$\frac{\partial\tau}{\partial s} = \frac{ds}{d\tau}$$

but by eq. 6-7  $\beta$  is inversely proportional to the square root of  $\tau$ . In this way the authors found the relation between  $\sqrt{\tau}$  and  $T$  shown in Fig. 11-3, which also shows in a striking manner the results of a completely different determination made by Shoenberg [Chap. 11 (d)].

Incidentally, all these measurements of the critical magnetic field when used in eq. 18-2 to calculate  $\beta$  lead to the expected result that, sufficiently far below the transition temperature,  $\beta$  has the order of magnitude of  $10^{-19}$  cm<sup>2</sup>.

(f) The whole argument of Chaps. 17 and 18 depends on the condition emphasized in Chap. 17 (a) that no current shall be entering or leaving the superconductor at the points of interest on its surface. It is only under this condition that the London stresses give rise to the tensile stress  $V_2/2\pi^2$  toward the interior of the superconductor. Where there is a current entering supplied from outside and where  $\mathbf{i}'$  has no tangential component, the tension is replaced by a pressure of the same amount directed outwards. In general if both normal and tangential components of  $\mathbf{i}'$  exist, the force is inclined to the surface. The tangential component is exactly zero only at a few points on the surface of a "thick" superconductor. For example we saw in Chap. 8 (d) that in a superconducting cylinder of radius  $R$  to which a current is supplied through a normally conducting cylinder of the same thickness, the tangential component  $i_\theta'$  almost everywhere over the interface greatly exceeds the normal component  $i_r'$  as long as  $\beta R \gg 1$ . Only in areas around these radii of extension  $\beta^{-1} = i_r' \gg i_\theta'$ .

For a "thin" cylinder or more generally a "thin" superconductor of arbitrary cross section in which the supercurrent, like the ohmic current

in the normal conductor, spreads uniformly over the cross section [Chap. 7 (a)], the tangential component at the interface vanishes. At such points, provided the normally conducting leads consist of the same material as the superconductor, thermodynamic equilibrium between the two phases would depend on the condition (compare eq. 17-3)

$$\frac{1}{2} (\mathbf{i}' \cdot \mathbf{G}) = \frac{(i_r' - i_\theta')}{V}$$

This condition cannot be satisfied, because at any temperature at which the superconductor can exist at all, i.e., any temperature below  $T_c$ ,  $i_r' - i_\theta' > 0$  according to Chap. 17 (e) and Fig. 17-1 whereas  $(\mathbf{i}' \cdot \mathbf{G})$  is positive according to Chap. 3. The current at the interface can therefore only strengthen the tendency of the superconductor to grow at the expense of the normal conductor. Certain as yet unexplained relaxation phenomena which often blur the sharpness of the phase transition may be related to this point.

### CHAPTER 19

#### The Intermediate State

(a) If the superconductivity of a specimen is quenched isothermally by an increasing external magnetic field, it does not transform immediately and completely into the normally conducting state. The nearest approach to a sudden complete transition is found with straight wires in longitudinal fields. However, even in this case the resistance does not change from zero to its final value in one single jump. The transition is by no means continuous, but takes place in several separate jumps. Thus if, following Justi, one wraps around the specimen an induction coil connected with an oscillograph or a telephone, and subjects the specimen to a continuously increasing magnetic field, one observes current impulses caused by sudden large changes in the flux of induction.

In other cases where the transition is much slower it can be followed through all its intermediate stages by placing a minute bismuth wire inside cavities in the specimen and measuring their resistance as a function of the external field. This was done by de Haas and his collaborators. The resistance of bismuth changes in a known manner with the local magnetic field strength. This arrangement, which naturally is limited to thick superconductors, demonstrates the gradual penetration of the external field. It is impossible for a normally conducting shell to form either completely or partly round a superconducting core. The thermodynamics of Chap. 17 requires the existence of the critical magnetic field  $H_c$ , corresponding to the prevailing

temperature at every point on the boundary between any such normal envelope and the core. On the other hand, the lines of force, according to electrodynamics, must be parallel to the boundary surface. These two requirements are mathematically inconsistent.

(b) In the first place it is out of the question for the normally conducting places (either curves or, at least points) on the boundary surface where the incident lines of force divide sharply into two lines parallel to the surface. (For a spherical core this would occur at the poles, see Fig. 1-5). The field strength at these points is zero according to potential theory because the field direction is indefinite, and so cannot equal  $H_c$ . Let us confine ourselves for the moment to two-dimensional problems. Let the boundary of the core  $S$  consist of two parts  $S_1$  and  $S_2$ , of which the core borders either on empty space or on a normal conductor of chemically different material and  $S_1$  on the normally conducting shell. Both  $S_1$  and  $S_2$  may consist of several separate sections. We assume each section to be an analytic curve, i.e., they can be represented by equations of the form  $x = f(y)$ ,  $y = g(z)$ , where  $f$  and  $g$  are analytic functions.

At each point where a section of  $S_1$  meets the adjacent section of  $S_2$  it is not permissible for them to form an angle with each other. Such an angle according to potential theory, would be zero; if the kink were raised (convex), the field would be extremely large (mathematically infinite); in any case it could not be equal to  $H_c$  at such kinks. The above parametric representation therefore holds uniformly over the whole boundary curve  $S$ , and therefore  $H$  on the boundary must also be an analytic function of the parameter  $s$ . As it is constant and equal to  $H_c$  over all parts of  $S$ , it must also be equal to  $H_c$  over  $S_1$  in spite of the fact that it must also be zero at some points.

The same inconsistency is found in the three-dimensional case. We can ascribe to any part of the boundary, whether it belongs to  $S_1$  or to  $S_2$  an analytical representation in terms of two parameters:  $\mathbf{x} = \mathbf{f}(s, t)$ ,  $\mathbf{y} = \mathbf{g}(s, t)$ ,  $\mathbf{z} = h(s, t)$ . No singularities are permitted at any point, where sections of  $S_1$  and  $S_2$  touch, because they would cause zeros or infinites in  $H$ . Therefore the analytical representation holds uniformly over the whole boundary  $S$ . Then  $H$  is also an analytical function of  $s$  and  $t$ . Because it is instant and equal to  $H_c$  over  $S_2$ , it must also be constant over  $S_1$ , in spite of the fact that places must exist where  $H = 0$ . So if a piece of material cannot be either normally conducting as a whole nor superconducting, it must be in an "intermediate state," representing a mixture of alternating superconducting and normally conducting regions.

The difficulty discussed above for thick superconductors does not exist for small superconducting regions dispersed through a normal conductor, because such small regions do not disturb the magnetic field, according to

Chap. 7, and are themselves barely affected by the field, according to Chap. 18.

These conclusions are confirmed by an experiment by Shubnikov and Nachitov.<sup>1</sup> They quenched the superconductivity of a sphere in a magnetic field and measured the electric resistance parallel and perpendicular to the external field before the sphere had become completely normally conducting. Long after resistance had appeared in the direction perpendicular to the field, they could find no resistance in the direction parallel to the field. This is difficult to explain except in terms of coexisting normal and superconducting regions. It suggests, moreover, that the superconducting regions are much more extended in the direction of the field than in the transverse direction. This fits in with the argument of Chap. 18 (b) according to which a cylinder or any other elongated specimen loses its superconductivity much more easily in a transverse field than in a longitudinal one.

(c) The earliest method of recognizing superconductivity was to observe the disappearance of the  $d - \sigma$  resistance. However, this method is hardly suitable for distinguishing between the superconducting and the intermediate states because the normally conducting regions will not participate in carrying the current so long as the current can find a closed path through the superconducting regions.

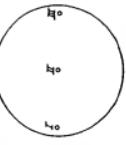
In order to observe the field penetration of Haas and Casimir-Jonker,<sup>2</sup> inserted minute bismuth wires, as described above, in holes in a thin wire 0.7 cm in diameter, see Fig. 19-1. They measured the increase of resistance of the bismuth wires while gradually increasing the external magnetic field  $H_x$ . Figure 19-2 shows the results when the plane of the wires is perpendicular to the field  $H_x$ . Fig. 19-3 when it is parallel. The critical value  $H_c$  can be recognized in both diagrams at the point where the resistance curves meet the resistance curve of a bismuth wire exposed to the external field  $H_x^0$  and indicated in Fig. 19-2 by the dotted line. This point is where the specimen allows the external field to penetrate it completely. In Fig. 19-2

Fig. 19-1. Cross section through tin cylinder with bismuth probe wires inserted at I, II, and III. (After W. J. de Haas and J. M. Casimir-Jonker.)

<sup>1</sup>L. Shubnikov and J. Nachitov, *J. Exp. Theor. Phys. (U.S.S.R.)*, 7, 566 (1937).

<sup>2</sup>W. J. de Haas, J. Voogd, and J. M. Casimir-Jonker, *Physica*, 1, 281 (1934).

<sup>3</sup>W. J. de Haas, and J. M. Casimir-Jonker, *Physica*, 1, 291 (1934).



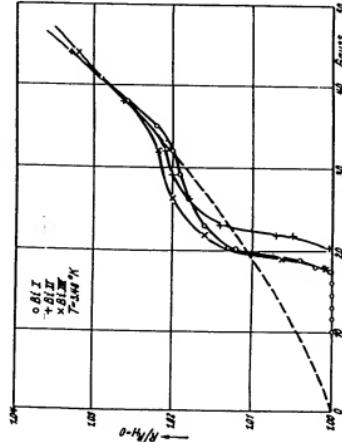


Fig. 19-2. Increase of resistance in the bismuth probe wires due to penetration of a magnetic field normal to the plane of the wires.

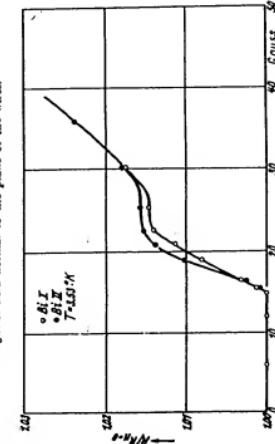


Fig. 19-3. Increase of resistance in the bismuth probe parallel to the plane of the wires.

$H_c$  falls at about 36 oersteds; in Fig. 19-3 at about 30 oersteds because of the slightly higher temperature. One sees that the first sign of the field penetration occurs in both diagrams at the field  $H^* = \frac{1}{2} H_c$ , i.e., at 18 and 16 oersteds, respectively, as required by theory. The wire II was placed in the axis of the wire, so the fact that its curve reacted only at 20 oersteds does not alter the fact that both the wires I and III, placed nearer the outside of the wire, show the breakdown of superconductivity already at 18 oersteds.

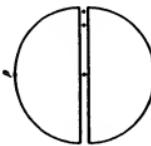


Fig. 19-4. Cross section of a tin sphere cut across an equatorial plane with an insulating plane with a bismuth wire inserted at the points shown. (After W. J. de Haas and O. A. Guineau.)

Fig. 19-5. Magnetically induced ionic thermal transition from super- to normal conduction in a single crystal tin sphere. Points marked A, B, C represent magnetic field strengths shown by the bismuth probes of Fig. 19-4. D the field strength at the pole P of the sphere.

The theory has been confirmed more exactly for the case of a sphere where, according to Chap. 18 (6) the critical value should be  $H^* = 2 H_c/3$ , de Haas and Guineau<sup>1</sup> cut a tin sphere (1.66 cm in diameter) into two hemispheres and placed them 0.03 mm apart (Fig. 19-4). In the space between the two halves they placed three bismuth wires, one in the center, the second 0.65 cm and the third 0.75 cm from the center. The field strengths calculated from the resistance decrease in the bismuth wires are shown in Fig. 19-5 as a function of  $H^*$  which in this experiment was perpendicular to the plane of the cut. The magnetic field strength at the pole P of the sphere is also plotted. The four curves coincide exactly. They start at 24 oersteds, and at 36 oersteds they join the straight line  $H = H^*$ , indicating that the protective influence of the tin sphere has completely disappeared. Thus the critical value  $H_c = 36$  oersteds, and the limiting value  $H^*$  for superconductivity is  $2/3 H_c$ .

<sup>1</sup>W. J. de Haas and O. A. Guineau, *Physica*, 8, 182 (1936).

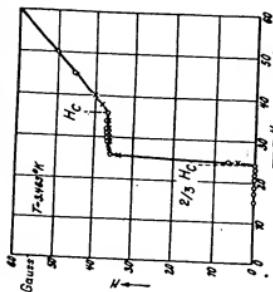


Fig. 19-6. Magnetically induced isothermal transition from super- to normal conduction of a single crystal tin sphere. The field strengths are measured in a hole bored through the center of the sphere parallel to the field.

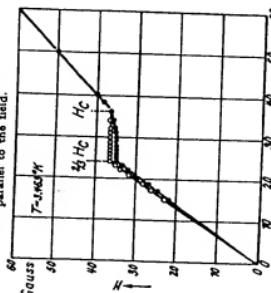


Fig. 19-7. Magnetically induced isothermal transition from super- to normal conduction in a single crystal tin sphere. Field strength first remains constant at a point on the equator of the sphere; ● solid strength at a point on the plane of the equator slightly outside the sphere.

This is further confirmed by experiments represented in Fig. 19-6,

in which the bismuth wires were placed inside a channel parallel to the field through the center of the sphere to measure the field penetration. The field jumps almost discontinuously to the value 36 oersteds when the external field reaches the value 24 oersteds, and remains practically constant until  $H_0$  also reaches the value 36 oersteds. From then on the sphere no longer disturbs the field, and it follows the line  $H = H_0$ .

Figure 19-7 explains why the field jumps immediately to 36 oersteds in spite of the fact that  $H_0$  is still smaller than this value. In this experiment two bismuth wires were placed in the equatorial plane, one exactly on the equator of the sphere (which was not cut like the one in Fig. 19-6), the other a little above the surface of the sphere. In this case, the measured field  $H$  follows a straight line  $H = 3H_0/2$  and shows the intensification of the field at the equator of a superconducting sphere [Chap. 11 (9)]. At  $H_0 = 24$ , and  $H = 36$  oersteds, however, the superconductivity breaks down, and  $H$  first remains constant at this value as shown in Fig.

19-6. As soon as  $H_0$  also reaches 36 oersteds the undisturbed field  $H^0$  exists throughout the sphere as shown again in this diagram.

The experiments represented in Figs. 19-4 and 19-5 have been repeated by Meshikowski and Shainikov with a considerably narrower slit. Also instead of three fixed bismuth wires they used a movable bismuth probe which they displaced continuously along the diameter, registering field strengths at each position. For wider slits and relatively thick bismuth probes they confirmed the results of Fig. 19-5. But with an especially thin slit, namely,  $1.2 \times 10^{-4}$  cm, in a spherical single crystal of tin 5.9 cm in diameter, they found large irregular fluctuations of the field strength, corresponding to the irregular distribution of normal and superconducting domains.

Figure 19-8 shows the results at 30 K, corresponding to a critical value of the field at 97 oersteds. Curve A shows the field distribution along a diameter when the external field  $H_0$  is less than (2/3)  $H_C$ , i. e., 65 oersteds. The sphere, being superconducting as a whole, completely excludes the field, but there is already a trace of the field  $H_0$  by only exceeds (2/3)  $H_C$  by 2 oersteds (curve B). The maxima showing this effect increase in number with increasing  $H_0$ . At  $H_0 = 94$  oersteds (curve G) the field has penetrated with the sphere almost completely, and at  $H_0 = 110$  oersteds it has the same value inside as outside the sphere.

The authors emphasize the fact that it is impossible to reproduce the curves exactly, although their general character remains the same with repeated experiments. The irregularity of the intermediate state is demonstrated by the accidental form of the field distribution.

A. Meshikowski and A. Shainikov, *J. Physics (U.S.S.R.)* 11 (1947).

## CHAPTER 20

A Nonlinear Extension of the Theory<sup>1</sup>

(a) According to Chap. 17 the breakdown of superconductivity becomes inevitable for thermodynamic reasons as soon as the energy density  $\frac{1}{2}(\mathbf{v} \cdot \mathbf{Q})$  reaches the critical value  $f/(w - s)/v$  at any point of the surface, the transformation into the normally conducting phase starting at that point (eq. 17-4). For a "thick" superconductor, we can, according to eq. 7-37 put  $\frac{1}{2}(\mathbf{v} \cdot \mathbf{Q}) = \frac{1}{2}H_0^2$ , and this leads to the critical value of the magnetic field strength given by eq. 17-36. However, the atomic theory of superconductivity recently developed by Heisenberg<sup>2</sup> leads to the idea of a maximum density of the supercurrent that cannot be exceeded because of quantum theoretical restrictions. The question arises: Is this a new stability condition for the superconducting phase? Is the breakdown of superconductivity possible from within, and how is this related with thermodynamics?

The maximum current density  $I_m$  like the critical magnetic field strength  $H_c$  must be a function of temperature. They are both zero at the transition temperature  $T_c$ . Also  $I_m$  is zero at absolute zero temperature, and has a maximum, according to current estimates, in the neighborhood of  $\sqrt{\epsilon}T_c$ . According to Chap. 1, Fig. 1-4, the critical field  $H_c$ , increases continuously with decreasing temperature. This different behavior emphasizes the importance of the following question: If the maximum total current, and therefore for a wire of given thickness the maximum total current, decreases toward zero with decreasing temperature, how can the supercurrent produce the field strength at the surface required by thermodynamics for the breakdown of superconductivity?

There is no upper limit to the current density in the theory so far presented in this book. We shall make it possible to include such a maximum current by means of a nonlinear extension of the theory without sacrificing many of its results. This step was also suggested by the fact that experimentalists have for some time doubted whether the penetration depth of a transverse field in a wire is actually independent of the field strength in the manner required for the theory of Chap. 9.\*

<sup>1</sup>Compare the following references:

M. V. Laut, *Ann. Phys.*, (6) 6, 197, 1949.

W. Heisenberg, (a) *Z. Naturforsch.*, 8a, 65 (1948); (b) *Z. Naturforsch.*, 8a, 185 (1949).

W. Heisenberg, *Math.-Phys. Klasse*, 1947, p. 25; (d) *Ann. Physik*, 8, 285 (1949).

H. Koppe, (a) *Z. Naturforsch.*, 4a, 79 (1949); (b) *Ergeb. exakt. Naturw.*, 88, 265, (1950).

See Heisenberg's reference in footnote 1.

\* Compare A. E. Pippard, *Proc. Roy. Soc. A* 208, 195, 210, (1950).

(b) We shall not change any of the fundamental equations enumerated in Chap. 3 except the relation between supercurrent density  $I$  and the supercurrent momentum  $\mathbf{Q}$ , i. e., we abandon eqs. VIII.1 and VIII.4, but retain all the other equations indicated by roman numerals. The new relation will be left open to a considerable extent, but being required that it shall be uniquely reversible and go over to the linear relation VIII.1 (or VIII.4) for sufficiently weak currents, that a change of sign of  $v$  shall cause a change of sign of  $G$ , and the angle between  $v$  and  $G$  shall always be acute so that

$$(\mathbf{v} \cdot \mathbf{Q}) > 0 \quad (20-1)$$

For a given direction of  $v$  the absolute value of  $G$  and the absolute value of  $v$  increase simultaneously.

The most important restriction, however, arises from the energy principle. Equation 5-4 can be taken over immediately, and by eq. IX we can put in that equation

$$(\mathbf{E} \cdot \mathbf{v}) = \left( \mathbf{v} \cdot \frac{\partial \mathbf{G}}{\partial t} \right) \quad (20-2)$$

We require that the integral

$$F = \int \left( \mathbf{v} \cdot \frac{\partial \mathbf{G}}{\partial t} \right) dt \quad (20-3)$$

shall depend only on the final supercurrent density when the latter is through at the beginning, being independent of the intermediate states through which it has passed. Owing to the assumption of unique reversibility of the relation between  $v$  and  $G$  we can also state that  $F$  depends only on the momentarily existing supercurrent momentum  $G$ , or alternatively, that the integral

$$F = \int_0^G (1 - dg) \quad (20-4)$$

shall be independent of the path of integration in  $G$ , space. Otherwise the theory would lead to energy transformations within the superconductor contradictory to observation. Under these conditions eq. 20-4 becomes the definition of the density of free energy  $F$ , associated with the supercurrent. The mathematical expression for these conditions is:

$$\frac{\partial g'}{\partial Q_p} - \frac{\partial v'}{\partial G_p} = 0 \quad (a, \beta = 1, 2, 3) \quad (20-5)$$

This ensures that the integral appearing in the equation

<sup>2</sup>In the integrated it is to be understood that  $v$  and  $G$  are variables of integration that assume the values  $v$  and  $G$  at the upper limit. The ratio between  $v$  and  $G$  is naturally the same as between  $v$  and  $G$ .

$$F_i = (I \cdot G) - \int_0^{\mu} (g \cdot dI) \quad (20-6)$$

shall be independent of the path of integration in  $I_s$  space and tends to conditions equivalent with eq. 20-5, namely,

$$\frac{\partial G_\alpha}{\partial I_\beta} - \frac{\partial G_\beta}{\partial I_\alpha} = 0 \quad (\alpha, \beta = 1, 2, 3) \quad (20-7)$$

From eq. 20-1 it then follows that

$$F_i > 0 \quad (20-8)$$

Equation 20-4 may now be integrated in  $G_o$  space along the straight line that connects the origin (zero  $G$ ) with the end of the vector  $G$ . One finds that increments  $dG_\alpha$  are proportional to  $dI_\alpha$  and have the same sign, so that  $(I \cdot dG) > 0$  along the whole path. The same argument applied to  $G_o$  proves that the integral in eq. 20-6 is positive. It therefore follows that

$$F_i < (I \cdot G) \quad (20-9)$$

The surfaces  $F_i = \text{constant}$  will be closed shells in both  $G_o$  space and about the origin as a center. As long as the linear approximation VII holds, eq. 20-7 goes over into the symmetry condition  $\frac{\partial G_\alpha}{\partial I_\beta} = \frac{\partial G_\beta}{\partial I_\alpha}$ , and the surfaces are ellipsoids or spheres for the cubic system. In the general case they have less simple forms, and in general  $I$  and  $G$  are different in direction even for rotation.  $G$  must do the same because of the uniqueness of their relationship. The possibility cannot be excluded that there exists a surface in  $I_s$  space, at a finite distance from the origin, corresponding to infinite free energy, there would exist a maximum current density dependent on direction. At such a surface  $G$  would also become infinite, for otherwise  $F_i$  must remain finite by eq. 20-9. Under these circumstances the energy principle (compare eq. 5-5) takes the form

$$\frac{3}{4} \left[ \frac{1}{2} E^2 + \frac{1}{2} H^2 + F_i \right] + (I^o \cdot E) + \epsilon \operatorname{div}(I^o \times H) = 0 \quad (20-10)$$

Just as in Chap. 5, we can conclude from this that space charges in a superconductor compensate each other in a short time, or move to the surface until the total density  $\rho = \rho^o + \rho'$  vanishes. We do not learn anything from this theory about  $\rho'$  itself.

By integrating the integral in eq. 20-6 along the same straight line in  $I_s$  space one can put

$$(g \cdot dI) = \left[ \frac{(g \cdot I)}{|I|} \right] d|I|$$

For the linear theory the component  $(g \cdot I)/|I|$  of the vector  $g$  in the direction  $I$  becomes proportional to  $|I|$ , as shown by the straight line in Fig. 20-1. We then find (in agreement with eq. 5-6)

$$\int (g \cdot dI) = \frac{1}{2} (G \cdot I), \quad F_i = \frac{1}{2} (I \cdot I) \quad (20-11)$$

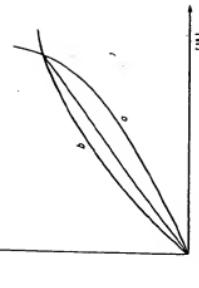


Fig. 20-1. Schematic representation of the types of nonlinear relations between supercurrent momentum  $G$  and supercurrent density  $I$ .  $A$  below the curve means that the supercurrent is greater than the mean value of the supercurrent in the direction of the supercurrent.  $B$ : Ordinate: component of supercurrent momentum in direction of the supercurrent.

In the nonlinear theory the relation between  $(E \cdot I)/|I|$  and  $|I|$  can be represented for example by a curve of the type of Fig. 20-1. Then clearly

$$\int (g \cdot dI) < \frac{1}{2} (G \cdot I), \quad F_i > \frac{1}{2} (G \cdot I) \quad (20-11)$$

while for a curve of the type  $b$  in Fig. 20-1 we would have

$$\int (g \cdot dI) > \frac{1}{2} (G \cdot I), \quad F_i < \frac{1}{2} (G \cdot I) \quad (20-12)$$

The existence of a maximum current density corresponds to the case  $a$  because here  $G$  increases more rapidly than proportional to  $|I|$ . (c) We now have to find out to what extent the results of the linear theory still apply, and we start with the Meissner effect.<sup>4</sup>

<sup>4</sup>The equation 7-4 is still valid because in proving it the relation between  $G$  and  $I$  is never used. However we cannot take over the proof of the uniqueness theorem following eq. 7-4 because the difference field between two possible fields is no longer itself a possible field, i. e., one that satisfies the fundamental equations.

Let us first consider, as in Chap. 7, the stationary state with all field quantities depending only on  $x_3$ . Because of  $\operatorname{div} \mathbf{H} = 0$  and  $\operatorname{div} \mathbf{G} = 0$ , we get as before  $\mathbf{I}_4 = 0$ ,  $\mathbf{H}_3 = 0$ , but  $\mathbf{G}_3$  is generally different from zero. Equation X, under this assumption, yields  $c \frac{d\mathbf{G}_1}{dx_3} = \mathbf{H}_1$

$$\rightarrow c \frac{d\mathbf{G}_1}{dx_3} = \mathbf{H}_1, \quad (20-13)$$

whereas from II,

$$\rightarrow \mathbf{I}_4 = c \frac{d\mathbf{H}_3}{dx_3}, \quad \mathbf{I}_4 = c \frac{d\mathbf{H}_1}{dx_3} \quad (20-14)$$

Elimination of  $\mathbf{H}$  leads to the partial differential equations

$$c^2 \frac{d^2 \mathbf{G}_1}{dx_3^2} = \mathbf{I}_4, \quad c^2 \frac{d^2 \mathbf{G}_3}{dx_3^2} = \mathbf{I}_4, \quad (20-15)$$

in which  $\mathbf{G}_1$  and  $\mathbf{G}_3$  have to be regarded as functions of  $\mathbf{I}_4$  and  $\mathbf{I}'_4$ , respectively. These equations replace the former differential equation  $d^2 \mathbf{I}_4 / dx_3^2 = 0$ . Taking the product of the first of these with  $\mathbf{G}_1$  and the second with  $\mathbf{G}_3$  and adding the results we obtain

$$\mathbf{G}_1 \frac{d^2 \mathbf{G}_1}{dx_3^2} + \mathbf{G}_3 \frac{d^2 \mathbf{G}_3}{dx_3^2} = \frac{1}{c^2} (\mathbf{I}_4 \cdot \mathbf{G})$$

and by eq. 20-13:

$$\begin{aligned} \frac{d^2}{dx_3^2} (\mathbf{G}_1^2 + \mathbf{G}_3^2) &= \frac{2(\mathbf{I}_4 \cdot \mathbf{G})}{c^4} + \left( \frac{d\mathbf{G}_1}{dx_3} \right)^2 + \left( \frac{d\mathbf{G}_3}{dx_3} \right)^2 \\ &= \frac{2(\mathbf{I}_4 \cdot \mathbf{G})}{c^4} + \frac{\mathbf{H}^2}{c^2}. \end{aligned} \quad (20-16)$$

On the other hand, if we multiply the left-hand equations of 20-13 and 20-14 together, and also the right-hand equations, and add the results, we find, by using eq. 20-4 that

$$\frac{d\mathbf{F}^2}{dx_3} = \frac{1}{2} \frac{d\mathbf{H}^2}{dx_3} \quad (20-17)$$

or, by introducing an arbitrary integration constant  $C$ ,

$$\mathbf{F}^2 = \frac{1}{2} \mathbf{H}^2 - C \quad (20-18)$$

Using eqs. 20-18 and 20-15 gives

$$\frac{d^2}{dx_3^2} (\mathbf{G}_1^2 + \mathbf{G}_3^2) = \frac{2}{c^2} [(\mathbf{I}_4 \cdot \mathbf{G}) + \mathbf{F}^2 + C] \quad (20-19)$$

Here  $(\mathbf{I}_4 \cdot \mathbf{G})$  and  $\mathbf{F}^2$  are to be regarded as known functions of  $\mathbf{I}_4$  and  $\mathbf{I}'_4$  just as are  $\mathbf{G}_1$  and  $\mathbf{G}_3$ .

In order to discuss eq. 20-19, we now write  $\mathbf{z}$  for  $x_3$ , and put  $\mathbf{G}_1 = \mathbf{G}_1(\mathbf{z})$  and  $\mathbf{G}_3 = \mathbf{G}_3(\mathbf{z})$ . To within the linear approximation  $(\mathbf{I}_4 \cdot \mathbf{G})$  as well as  $\mathbf{F}^2$  are proportional to  $(\mathbf{G}_1^2 + \mathbf{G}_3^2)$ , the proportionality factor depending on the ratio  $G_1/G_3$ . In any case, on this approximation eq. 20-19 assumes the form

$$\mathbf{z}'' = \mathbf{A}^2 (\mathbf{u} + C')$$

where  $A$  is a constant and  $C'$  another constant proportional to  $C$ . The solution in terms of another integration constant  $B$  is

$$\mathbf{u} + C' = \operatorname{Exp} [\pm A (z - z_0)]$$

We use the lower sign and choose  $C = 0$ , therefore also  $C' = 0$ . Then  $\mathbf{u}$  and therefore also  $\mathbf{G}_1$  and  $\mathbf{G}_3$  approach zero with increasing  $z$ . By eqs 20-13 and 20-14  $\mathbf{H}$  and  $\mathbf{H}'$  decrease exponentially with increasing  $z$ , in agreement with Chap. 7. However,  $(\mathbf{G}_1^2 + \mathbf{G}_3^2)$  increases in the negative  $z$  direction because of the positive  $\mathbf{u}'$ , finally without limit. It depends upon the relation between  $\mathbf{p}$  and  $\mathbf{G}$  whether  $\mathbf{u}$  increases without limit at a finite  $z$  or only at infinite  $z$ . In any case we can, by choosing a suitable value for  $z_0$ , arrange for  $\mathbf{G} = \mathbf{c}^2 [((\mathbf{G}_1^2 + \mathbf{G}_3^2) + (d\mathbf{G}_1/dx_3)^2)]$  to have any prescribed value  $\mathbf{H}(0)$  at  $z = z_0 = 0$ . We obtain also a prescribed direction for  $\mathbf{H}$  at the origin we must also be free to choose the ratio  $G_1/G_3$  at any point appropriately.

Let the superconductor occupy the half space  $x_3 > 0$  as in Chap. 7, while a homogeneous magnetic field  $\mathbf{H}_0$  exists where  $x_3 < 0$ . Then the solutions just discussed will yield the Meissner effect, i. e., the restriction of the magnetic field in the superconductor to a protecting layer close under the surface.

For a plane parallel plate of finite thickness,  $C$  differs from zero. Indeed  $C < 0$  if a current is passed through the plate without producing an additional magnetic field. Then  $\mathbf{H} = 0$  exactly at the center of the plate, by symmetry, but  $\mathbf{p}$  and if  $F$  are different from zero. If instead we prescribe that the magnetic field  $\mathbf{H}$  shall be the same at the two surfaces without passing a current through it, then  $\mathbf{p} = 0$  but  $H$  differs from zero and therefore  $C > 0$  at the middle.<sup>6</sup>

<sup>6</sup>H. Kopp (see footnote 1) integrated the differential equation under the arbitrary assumption that

$$\mathbf{q} = \frac{\lambda \mathbf{p}}{\sqrt{1 - p^2/c^2}}$$

His result is represented in Fig. 20-2, which shows the field distribution in the superconducting half of space,  $x > 0$ . In this figure

$$\begin{aligned} \mathbf{i} &= \frac{|\mathbf{p}|}{c} \frac{\mathbf{p}}{\sqrt{1 - p^2/c^2}}, & H &= \frac{H_0}{\sqrt{1 - p^2/c^2}} \\ \mathbf{f} &= \frac{G}{c \sqrt{1 - p^2/c^2}}, & w &= \frac{w_0}{\sqrt{1 - p^2/c^2}} \end{aligned}$$

the unit for  $\mathbf{p}$  is  $\operatorname{Exp} [\pm A(z - z_0)]$ . The boundary surface of the superconductor has to be so chosen that it coincides with the prescribed value of  $H_0$ . If this value is comparatively small, the boundary lies fairly far to the left in the diagram and the field quantities decrease rapidly with increasing  $x$ . If  $H_0$  is relatively large, the boundary lies far to the right and the current density  $\mathbf{i}$  in the protecting layer is not much less than  $i_0$  over a wide region.

(d) In a cylinder carrying a current (Chap. 8) the situation becomes rather complicated unless the direction of the current coincides with a crystallographic axis of rotation, so that, by section (b), the vectors  $G$  and  $H$  are parallel. In this case we can use simply the magnitudes  $G$  and  $H$ .

Introducing the cylindrical coordinates as in Chap. 8,  $G$  and  $H$  become functions of the radius vector only. The same is true of the component of the magnetic field  $H_\theta$  in the  $\theta$  direction. Equation X then yields,

$$\frac{dG}{dr} = \frac{c}{r} \frac{d(H_\theta)}{dr}, \quad (20-20)$$

and from eq. II<sub>r</sub> (compare eq. 8-1)

$$\dot{\nu} = \frac{c}{r} \frac{d(rH_\theta)}{dr}. \quad (20-21)$$

We proceed as in section (c). Eliminate  $H$  and multiply the last two equations, and we then obtain

$$\frac{d}{dr} \left( r \frac{dG^2}{dr} \right) = \frac{2r}{C} (G^2 + H_\theta^2) \quad (20-22)$$

$$r \frac{dG^2}{dr} = \frac{2}{C} \int_0^r (G^2 + H_\theta^2) dr \quad (20-23)$$

and after integration

$$F_r = \frac{1}{2} H_\theta^2 + \int_0^r \frac{H_\theta^2}{r} dr + F'_r \quad (20-24)$$

The integration constant  $F'_r$  represents the energy density at the axis  $r = 0$ . According to eq. 20-22,  $dG/dr > 0$ , and this represents the Meissner effect.

Apply eq. 20-22 at the surface of the wire ( $r = R$ ) where the field is  $H^0$ . If  $R$  is large compared with a suitably defined penetration depth  $d$ , then the integral is at most of the order of magnitude  $(H^0)^2 d/R$ , and therefore small compared with  $\frac{1}{2} C H_\theta^2$ . The same is true of  $F_r$ . Consequently just as in eq. 20-18 where  $C = 0$  for the "thick" superconductor,

$$F_r = \frac{1}{2} (H^0)^2 \quad (20-24)$$

However, it is possible for  $F_r \gg \frac{1}{2} (H^0)^2$ , if  $F'_r \gg \frac{1}{2} C H_\theta^2$ , i.e., if the current is more or less uniformly distributed over the cross section of the cylinder.

(e) London's theories concerning persistent currents (eqs. 12-11 and 12-15) remain unchanged. The proof of these equations does not use any relation between  $G$  and  $H$ . Likewise eq. 12-21 is still valid; the left-hand side is still positive for any really existing field. Thus on the nonlinear theory there still exist no magnetic fields that are not produced by one of the three following causes: annular currents in a superconductor, ohmic currents in

a normal conductor, and permanent magnetism. The proof that these causes determine the field uniquely cannot be given in the same way as in Chap. 12, because now the difference field is no longer a possible field as it was in the linear theory.

(f) Sections (c) to (e) show how little the nonlinear theory differs from the linear one for stationary fields. It is difficult to decide between them on the basis of experimental evidence at present available. The decisive depending on the nonlinear theory there also exists a stress tensor  $G_{ij}$ , force on a homogeneous superconductor in Chap. 13 and exerting a volume to the Maxwell stress tensor. The fact that the resistance vanishes demands this unequivocally.

We now proceed to prove the impulse theorem 13-10 for the nonlinear theory. The force equation

$$G_{\alpha\beta} = l_\alpha' G_\alpha - \delta_{\alpha\beta} F_i \quad (20-25)$$

provides the required proof, because usually it does not differ from eq. 13-1 if we write  $P = l_\alpha$ ,  $Q = Q_\alpha$ , because then  $F_i = \frac{1}{2} Z_{i\alpha} Q_\alpha$ . The proof follows the earlier calculation of  $\operatorname{div} \Theta$ . We have to put  $x_1$  component of this vector is defined in eq. 13-3, and we have to put

$$G_{11} = l_1' G_1 - F_1, \quad G_{1\alpha} = l_\alpha' G_1, \quad G_{\alpha 1} = l_1 G_\alpha. \quad (20-26)$$

The differential coefficient  $dG^2/dx_1$  appears in the result.  $F_0$  depends both on  $v$  and on certain parameters  $\rho_\alpha$  which are present also in the relation between  $G$  and  $v$ . The  $\rho_\alpha$ 's are functions of the temperature and differ from substance to substance. Whenever the superconductor is inhomogeneous, whether due to temperature differences or to differences in chemical composition (as in alloys at solidified boundaries), the  $\rho_\alpha$ 's are functions of the coordinates  $x$ . From eq. 20-4 it therefore follows that

$$\frac{\partial F_i}{\partial x_1} = \sum_a l_{a1}' \frac{\partial Q_a}{\partial x_1} + \sum_{\alpha,y} \frac{\partial \rho_\alpha}{\partial x_1} \int_{\alpha,y}^0 \frac{\partial G_\alpha}{\partial x_1} dx_y. \quad (20-26)$$

The suffix  $g$  indicates differentiation at constant  $g$ . Using eq. 20-26 the calculation yields

$$\operatorname{div}_1 \Theta = \sum_{\alpha=1}^6 B_\alpha \quad (20-26)$$

where

$$B_1 = l_1 \frac{\partial G_1}{\partial x_1}, \quad B_2 = g_1 \frac{\partial l_1'}{\partial x_1}, \quad B_3 = -l_1 \frac{\partial G_1}{\partial x_1},$$

$$B_4 = -l_1 \frac{\partial G_1}{\partial x_1}, \quad B_5 = -l_4 \frac{\partial G_3}{\partial x_1},$$

$$B_6 = -\sum_{\alpha,y} \frac{\partial \rho_\alpha}{\partial x_1} \int_{\alpha,y}^0 \left( \frac{\partial l_\alpha}{\partial x_1} \right) dx_y. \quad (20-26)$$

$$B_1 = i_1 \frac{\partial G_1}{\partial x_2}, \quad B_2 = G_1 \frac{\partial i_1}{\partial x_2}$$

$$B_3 = i_3 \frac{\partial G_3}{\partial x_2}, \quad B_{10} = G_3 \frac{\partial i_1}{\partial x_3}$$

One sees at once that

$$B_1 + B_2 = 0, \quad B_1 + B_3 + B_{10} = i_1 \operatorname{curl}_1 G$$

$$B_1 + B_2 = -i_1 \operatorname{curl}_1 G, \quad B_3 + B_{10} = i_3 \operatorname{curl}_3 G$$

Therefore

$$\operatorname{div} \theta = G \operatorname{div} \nu - [i_1 \times \operatorname{curl} G] - \sum_{n,y} \operatorname{grad} p_n \int_0^a \left( \frac{\partial i_n}{\partial p_n} \right)_x d\delta_y, \quad (20-27)$$

This agrees with eq. 13-5 apart from the form of the term representing inhomogeneity. The argument following eq. 13-5 in Chap. 13 does not make use of the relation between  $G$  and  $i$ , and therefore applies in the present case and leads to the impulse theorem (compare eq. 13-10)

$$-\operatorname{div} [T(E) + T(H) + \theta] = \rho^0 E + \frac{1}{c} [i^0 \times H] +$$

$$+ \sum_{n,y} \operatorname{grad} p_n \int_0^a \left( \frac{\partial i_n}{\partial p_n} \right)_x d\delta_y + \frac{2}{c} \left[ \frac{1}{c} [E \times H] + \mu^0 G \right] \quad (20-28)^*$$

The whole discussion that follows the impulse theorem concerning the volume forces and the torque due to asymmetry of the tensor  $\theta_{10} = G_{10} = [G \times i_1]$ , etc.

remains valid here. The new fact that arises is that this asymmetry appears now even in cubic crystal superconductors, at least when we go beyond the region where the linear approximation is sufficient.

(f) Differences from the linear theory appear when we discuss the individual stress components. If we choose the  $x_1$  direction parallel to  $\nu$ , that

\*From eq. 20-8 it follows by differentiation with respect to  $p_n$  at constant  $\nu$  and  $G$

$$\sum_y \int_0^a \left( \frac{\partial i_y}{\partial p_n} \right)_x d\delta_y = - \sum_y \int_0^a \left( \frac{\partial \delta_y}{\partial p_n} \right)_x d\delta_y$$

$$-\sum_{n,y} \operatorname{grad} p_n \int_0^a \left( \frac{\partial \delta_y}{\partial p_n} \right)_x d\delta_y$$

The third term on the right-hand side of eq. 20-28 can therefore also be written in the alternative form given by M. von Laue (footnote 1)

In so far as  $F_\nu = \frac{1}{c} (\nu \cdot \mathbf{f})$ , this agrees with eqs. 17-3 and 17-4. For very thick specimens we can write  $\frac{1}{c} (\nu \cdot \mathbf{f})^0$  for  $F_\nu$ , by eq. 20-24 and so get exactly the forms 17-6 and 17-7 for the equilibrium conditions. As the whole of thermodynamics of this transition can be derived from this condition, according to Chap. 17, it remains unaffected by altering the electrodynamics in the above manner. If a plate of finite thickness however,  $C > 0$  in eq. 20-18 by section (e). If the magnetic field on both sides of the plate has the critical value  $H_c$ , then by eq. 20-31,  $F$  at the boundary has a lower value than the critical one. We then have to increase the external field to bring  $F_\nu$  to its critical value. This agrees qualitatively with the results of Chap. 18, which however no longer hold quantitatively in the nonlinear theory. The results depend on the relation between  $G$  and  $\mathbf{f}$  so that it should in principle be possible to derive conclusions about this relation from experimental data on the dependency of the critical magnetic field on the thickness of the plate.

(h) We now turn to the case where there does exist a maximum current density  $i_m$ , i.e., the family of surfaces in  $\nu$  space converge upon a finite surface on which  $F_\nu$  becomes infinite.

We consider first the superconductor of section (e), occupying half of

at some point in space, four of the nine components of  $\theta$  vanish there and the others have the values:

$$\theta_{11} = [i \cdot \mathbf{f}] - F_\nu, \quad \theta_{12} = \theta_{13} = -F_\nu, \quad \theta_{14} = i_1 \cdot G_3, \quad (20-29)$$

The components  $\theta_{11}$  and  $\theta_{31}$  also vanish if  $\nu$  and  $G$  are parallel, and then the current line is, as before, one of the principal axes of rotational symmetry of the tensor  $\theta$ . A tension  $F$  acts perpendicular to the current line, and a pressure is exerted on it because  $\theta_{12} = \theta_{13} < 0$  while  $\theta_{11} > 0$  according to eqs. 20-8 and 20-9. However, the pressure is no longer equal to the tension, but, by eq. 20-11 is smaller than the tension when  $G$  and  $\nu$  are related as in curve  $a$  of Fig. 20-1, and greater for the curve  $b$ .

In any case, according to eq. 20-29 a supercurrent flowing parallel to the surface of a superconductor must exert a force that has both a tangential and a normal component across the surface into the interior amounting to  $F_\nu$  per unit area. The work done by this field upon a surface element  $d\delta$  displaced a distance  $\Delta$  toward the interior of the superconductor amounts therefore to  $F_\nu \Delta d\delta$ . Therefore the thermodynamic equilibrium condition at the boundary between normally and superconducting phases of the same substance is (compare Chap. 17)

$$F_\nu = \frac{[i \cdot \mathbf{f}] - F_\nu}{V} \quad (20-30)$$

while at the free (outside) surface of the superconductor

$$F_\nu \leq \frac{[i \cdot \mathbf{f}] - F_\nu}{V} \quad (20-31)$$

always be done by choosing the appropriate direction for the coordinates  $x_1$  and  $x_2$ , but not as in Chap. 7 (exponentially in one way or another) but much more slowly, becoming a linear function of  $x_2$  (compare Fig. 20-13, H<sub>s</sub>) thus becomes layer to become thicker than one in the linear theory. As a matter of fact, to completely shield the field H<sub>0</sub> the Maxwell theory would require a total surface current  $\sigma H_0$ , and this, when the current density is limited, would have to be distributed over a thicker protecting layer. The penetration depth therefore becomes greater than in the linear theory and dependent on H<sub>0</sub>.

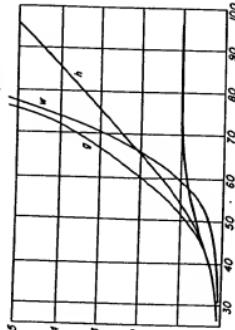


Fig. 20-2. Field distribution in the superconductor filling half space,  $x_1 > 0$ , according to Koppe (see footnote 1, Chapter 20). Abscissas:  $x_2$  in units of  $\exp \frac{H_0}{F_0}$ . Ordinate:  $h = H/\sqrt{F_0}$ ,  $w = F^2/\lambda_{\infty}^2$ .

$$\begin{aligned} i &= |v|/i_{\text{max}}, \\ \mathbf{f} &= G/v \sqrt{\lambda_{\infty}}, \end{aligned}$$

When a cylinder of radius R (section 2) carries a current, the field  $H_0$  at the surface is definitely less than the value  $R^2/c$  that would exist if the current density were equal to  $i_{\text{c}}$  over the whole cross section. In spite of this limitation on  $F^2/F_0$  can by eq. 20-25 attain any value at the surface, including the critical value given by eq. 20-51, so long as  $F_0'$  already has approximately this value, i. e., so long as the current is somewhat uniformly distributed over the cross section. But  $F_0'$  is nowhere so great as it is at the surface, and it is there that the greatest danger to the superconductivity lies, and it is also there that the breakdown starts as soon as  $F_0'$  reaches the critical value. This is true no matter how great the critical value may

<sup>†</sup>The same conclusion can be drawn from eq. 20-18 with  $C < 0$ .

be or how small the maximum current density. The upper limit of the current density is therefore not a new condition for the stability of the supercurrent; the thermodynamic relations 20-30 or 20-51 are still necessary and sufficient.

(i) Although the nonlinear theory agrees at least qualitatively, and in many important problems even quantitatively, with the linear theory for all stationary fields, in discussing oscillatory fields the linear theory can only be regarded as an approximation for oscillations of sufficiently small amplitude.

#### APPENDIX

##### Proof of Equation 14-8

If matter undergoes an arbitrary but continuous displacement  $\mathbf{u}$  then the change  $dP$  of an arbitrary vector P at a moving (material) point is related with the change  $d\mathbf{P}$  at a given point in space through the equation

$$\begin{aligned} dP_a &= \partial P_a + \sum_v \partial u_v \frac{\partial P_a}{\partial x_v} + \frac{1}{2} [\mathbf{P} \times \operatorname{curl} \mathbf{u}]_a \\ d(P_x P_y) &= \partial(P_x P_y) + P_x \left[ \sum_v \partial u_v \frac{\partial P_y}{\partial x_v} + \frac{1}{2} [\mathbf{P} \times \operatorname{curl} \mathbf{u}]_y \right] \\ &\quad + P_y \left[ \sum_v \partial u_v \frac{\partial P_x}{\partial x_v} + \frac{1}{2} [\mathbf{P} \times \operatorname{curl} \mathbf{u}]_x \right]. \end{aligned}$$

Therefore

$P_x P_y$  are the components of a symmetrical tensor, say  $t_{xy}$ . For the most general formulation of the symmetrical tensor we have to combine three noncoplanar vectors  $P_x, P_y, P_z$  as follows:

$$P_x P_y + Q_x Q_y + R_x R_y$$

The two additional terms do not alter the form of the transformation of  $dP_a$  into  $d\mathbf{P}_a$ , so we confine ourselves to the definition  $t_{xy} = P_x P_y$ .

Transcribing (a) we then have

$$d_{11} = \partial_{11} + \sum_v \partial_{1v} \frac{\partial_{11}}{\partial x_v} + \frac{1}{2} [(i_{12} \operatorname{curl}_3 \mathbf{u} - i_{13} \operatorname{curl}_2 \mathbf{u})]$$

<sup>4</sup> According to the above considerations (see M. von Laue, footnote 1), Stetze's hypothesis [compare Chap. 1 (e)] is now valid only for sufficiently "thick" superconductors.

$d_{13} = \partial_{13} + \sum_y \partial_{1y} \frac{\partial_{1y}}{\partial x_y} + \frac{1}{2} ((f_{13} - f_{12}) \operatorname{curl}_1 \hat{u}_1 + f_{12} \operatorname{curl}_2 \hat{u}_2 - f_1 \operatorname{curl}_3 \hat{u}_3)$   
etc.

Just as in Chap. 14 we now assume that all the  $d_{\alpha\beta}$ 's are zero so that

$$\partial_{11} = - \sum_y \partial_{1y} - \frac{1}{2} (f_{13} \operatorname{curl}_3 \hat{u}_2 - f_{12} \operatorname{curl}_3 \hat{u}_1) \quad (b)$$

Let  $\hat{Q}$  be another arbitrary vector. In (b) collect all the terms with  $\operatorname{curl}_1 \hat{u}_1$ , all those with  $\operatorname{curl}_2 \hat{u}_2$  and all those with  $\operatorname{curl}_3 \hat{u}_3$ , and obtain

$$\frac{1}{2} \sum_{\alpha\beta} Q_\alpha Q_\beta \partial_{\alpha\beta} = \frac{1}{2} Q_1^2 \partial_{11} + \cdots + Q_3 Q_3 \partial_{33} + \cdots =$$

$$- \frac{1}{2} \sum_{\alpha\beta} Q_\alpha \frac{\partial_{\alpha\beta}}{\partial x_y} \partial_{1y} + \frac{1}{2} (\operatorname{curl}_1 \hat{u}_1 [(Q_3^2 - Q_2^2) \partial_{13} + Q_1 Q_2 \partial_{12} - Q_1 Q_3 \partial_{23} + Q_2 Q_3 \partial_{12}])$$

$$+ \operatorname{curl}_2 \hat{u}_2 [\text{a similar factor to the above}]$$

$$+ \operatorname{curl}_3 \hat{u}_3 [\text{a similar factor to the above}]$$

This equation can be simplified by introducing the following vector:

$$\mathbf{R}_e \equiv \sum_\beta l_{\alpha\beta} Q_\beta$$

We then obtain

$$\frac{1}{2} \sum_{\alpha\beta} Q_\alpha Q_\beta \partial_{\alpha\beta} = - \frac{1}{2} \sum_\beta Q_\beta \Psi_\beta (\hat{u}_\alpha \cdot \nabla' f_{\alpha\beta} + \frac{1}{2} (\operatorname{curl} \hat{u}_\alpha \cdot \mathbf{R} \times \mathbf{Q})) \quad (c)$$

Finally writing  $\hat{u}$  in place of  $Q$  for  $R$  and  $\lambda_{\alpha\beta}$  for  $f_{\alpha\beta}$  we confirm eq. 14-8.

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**BRIEF ATTACHMENT AU**

NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

CROSS REFERENCE TO RELATED APPLICATION

see serial 8/87

DESCRIPTION

(B)

Technical Field

5 This invention relates to a new class of superconducting compositions having high superconducting transition temperatures and methods for using and preparing these compositions, and more particularly to superconducting compositions including copper and/or other transition metals, the compositions being characterized by a superconducting phase and a layer-like structure.

10

Background Art

15 Superconductivity is usually defined as the complete loss of electrical resistance of a material at a well-defined temperature. It is known to occur in many materials, including about a quarter of the elements of the periodic table and over 1000 alloys and other multi-component systems. Generally, superconductivity

is considered to be a property of the metallic state of  
a material since all known superconductors are metallic  
under the conditions that cause them to be supercon-  
ducting. A few normally non-metallic materials, for  
example, become superconducting under very high pressure  
wherein the pressure converts them to metals before they  
exhibit superconducting behavior.

5

Superconductors are known to be very attractive for the  
generation and energy-saving transport of electrical  
power over long distances, and as materials used to form  
the coils of very strong magnets. These magnets are used  
in, for example, plasma and nuclear physics, nuclear  
magnetic resonance medical diagnosis systems, and in  
connection with the magnetic levitation of fast trains.  
10 Other potential uses of superconducting materials occur  
in power generation systems using thermonuclear fusion  
where very large magnetic fields must be provided,  
superconducting magnets being the only possible means  
for providing such high fields. In addition to these  
15 applications, superconductors are known in high speed  
switching devices, such as Josephson type switches, and  
in high density packaging and circuit layouts. Super-  
conductors also are used in different types of elec-

10

15

20

tronic instrumentation, such as magnetic susceptometers  
and magnetometers.

While the advantages of superconductors are quite obvious to scientists and engineers, the common disadvantage of all presently known superconductive materials lies in their very low transition temperature. This temperature is often called the critical temperature  $T_c$  and is the temperature above which superconductivity will not exist. Usually  $T_c$  is on the order of a few degrees Kelvin. The element with the highest  $T_c$  is niobium whose  $T_c$  is  $9.2^{\circ}\text{K}$ . The composition having the highest previously known  $T_c$  is  $\text{Nb}_3\text{Ge}$  which exhibits a  $T_c$  of about  $23^{\circ}\text{K}$  at ambient pressure. Transition metal alloy compounds of the A15( $\text{Nb}_3\text{Sn}$ ) and B1( $\text{NbN}$ ) structure have been shown to have high superconducting transition temperatures.  
Among the A15 compounds is the aforementioned composition  $\text{Nb}_3\text{Ge}$ . Some of these compositions are described in J. Muller, Rep. Prog. Phys. 43, 663 (1980), and M. R. Beasley et al, Phys. Today, 37 (10), 60 (1984).

It is known in the art that a small number of oxides will exhibit superconductivity. Reference is made to D.C. Johnston et al, Mat. Res. Bull. 8, 777 (1973), which describes high temperature superconductivity in the Li-

5        *Answered 8/15/87*

Ti-O system with superconducting onsets as high as 13.7°K. These materials have multiple crystallographic phases including a spinel structure exhibiting the high  $T_c$ . Other metallic oxides, such as the perovskite Ba-Pb-Bi-O system, can exhibit superconductivity due to high electron-phonon coupling in a mixed valent compound, as described by G. Binnig et al, Phys. Rev. Lett., 45, 1352 (1980), and A.W. Sleight et al, Solid State Communications, 17, 27 (1975).

10      As is evident from the foregoing, superconductors presently known require liquid helium for cooling and this, in turn, requires an elaborate technology and a considerable investment in cost and energy. Accordingly, it is a primary object of the present invention to provide 15 new compositions which exhibit high  $T_c$  and methods for using and producing the same.

20      It is another object of the present invention to provide new superconducting compositions and methods for using and making them where cooling with liquid helium is not required in order to have superconductive properties in the compositions.

It is another object of the present invention to provide novel superconductive materials that are multi-valent oxides including transition metals, the compositions having a perovskite-like structure.

5 It is a further object of the present invention to provide novel superconductive compositions that are oxides including rare earth and/or rare earth-like atoms, together with copper or other transition metals that can exhibit mixed valent behavior.

10 It is a still further object of the present invention to provide novel superconductive compositions exhibiting high  $T_c$ , where the compositions are oxides including a phase having a layer-like structure and including copper.

15 It is a still further object of the present invention to provide new superconductive compositions exhibiting high  $T_c$ , where the superconductive compositions include layered structures including a rare earth and/or rare earth-like element and a transition metal.

20 It is another object of this invention to provide a new class of superconducting compositions characterized by

a  $T_c$  greater than 26 °K, and methods for making and using these compositions.

It is another object of this invention to provide new compositions and methods for using them, where the compositions include a multi-valent oxide of copper and exhibit a  $T_c$  greater than 26°K.

5

The basis for our invention has been described by us in the following previously published article: J.G.

10 *H. Bednorz  
8/5/81*  
Bednorz and K.A. Muller, Zeitschrift fur Physik B -  
Condensed Matter, 64, pp. 189-193, (1986)

Another article of interest by us is J.G. Bednorz, K.A. Muller, M. Takashige, Europhysics Letters, 3(3), pp. 379-385 (1987).

#### Summary of the Invention

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This invention relates to novel compositions exhibiting superconductivity at temperatures higher than those obtained in prior known superconductive materials, and to methods for using and forming these compositions. These compositions can carry supercurrents (i.e., electrical

*Ann D*  
*8/15/87*

currents in a substantially zero resistance state of the composition) at temperatures ~~at~~ greater than 26°K. In general, the compositions are characterized as mixed transition metal oxide systems where the transition metal oxide can exhibit multivalent behavior. These compositions have a layer-type crystalline structure, often perovskite-like, and can contain a rare earth or rare earth-like element. A rare earth-like element (sometimes termed a near rare earth element) is one whose properties make it essentially a rare earth element. An example is a group IIIIB element of the periodic table, such as La. Substitutions can be found in the rare earth (or rare earth-like) site or in the transition metal sites of the compositions. For example, the rare earth site can also include alkaline earth elements selected from group IIA of the periodic table, or a combination of rare earth or rare earth-like elements and alkaline earth elements. Examples of suitable alkaline earths include Ca, Sr, and Ba. The transition metal site can include a transition metal exhibiting mixed valent behavior, and can include more than one transition metal. A particularly good example of a suitable transition metal is copper. As will be apparent later, Cu- oxide based systems provide unique and excellent properties as high  $T_c$  superconductors.

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An example of a superconductive composition having high  
5  $T_c$  is the composition represented by the formula  
RE-TM-O, where RE is a rare earth or rare earth-like  
element, TM is a nonmagnetic transition metal, and O is  
oxygen. Examples of transition metal elements include  
10 Cu, Ni, Cr etc. In particular, transition metals that  
can exhibit multi-valent states are very suitable. The  
rare earth elements are typically elements 58-71 of the  
periodic table, including Ce, Nd, etc. If an alkaline  
15 earth element (AE) were also present, the composition  
would be represented by the general formula RE-AE-TM-O.

The ratio (AE,RE) : TM is generally approximately 1:1,  
but can vary from this as will be shown by examples where  
the ratio (AE,RE) : TM is 2:1. Of course, the amount  
of oxygen present in the final composition will adjust  
depending upon the processing conditions and will be  
such that the valence requirements of the system are  
satisfied.

20 The methods by which these superconductive compositions  
can be made can use known principles of ceramic fabri-  
cation, including the mixing of powders containing the  
rare earth or rare earth-like, alkaline earth, and

transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air.

A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal. Copper can exist in a Cu<sup>2+</sup> or Cu<sup>3+</sup> mixed valence state. The state(s) assumed by copper in the overall composition will depend on the amount of oxygen present and on any substitutions in the crystalline structure. Very high T<sub>c</sub> has been found in Cu-oxide systems exhibiting mixed valence states, as indicated by conductivity and other measurements. Copper oxide systems including a rare earth or rare earth-like element, and an alkaline earth element, are unique examples of this general class of superconducting layered copper oxides which exhibit T<sub>c</sub> greater than 26°K.

These and other objects, features, and advantages will be apparent from the following more particular description of the preferred embodiments.

Brief Description of the Drawings

FIG. 1 is a schematic illustration of a representative circuit used to measure dc conductivity in the high  $T_c$  superconductors of this invention.

5 FIG. 2 is a plot of the temperature dependence and resistivity in the composition  $Ba_x La_{5-x} Cu_5 O_5(3-y)$  for samples with  $x(Ba)=1$  (upper two curves, left scale) and  $x(Ba)=0.75$  (lower curve, right scale). The influence of current density through the composition is also shown.

10 FIG. 3 is a plot of the low temperature dependence of resistivity in the composition  $Ba_x La_{5-x} Cu_5 O_5(3-y)$  with  $x(Ba)=1$ , for different annealing conditions (i.e., temperature and oxygen partial pressure).

15 FIG. 4 is a plot of the low-temperature resistivity of the composition  $Ba_x La_{5-x} Cu_5 O_5(3-y)$  with  $x(Ba)=0.75$ , recorded for different densities of electrical current through the composition.

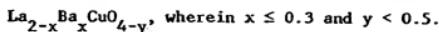
Description of the Preferred Embodiments

The superconductive compositions of this invention are transition metal oxides generally having a mixed valence and a layer-like crystalline structure, and exhibit  $T_c$ 's higher than those of previously known superconducting materials. These compositions can also include a rare earth site in the layer-like structure where this site can be occupied by rare earth and rare earth-like atoms, and also by alkaline earth substitutions such as Ca, Sr, and Ba. The amount of oxygen present will be such that the valence requirements of the system are satisfied, the amount of oxygen being somewhat a function of the processing steps used to make the superconductive compositions. Non-stoichiometric amounts of oxygen can be present in these compositions. The valence state of the elements in the oxide will be determined by the final composition in a manner well known to chemists. For example, the transition metal Cu may be present in some compositions in both a  $Cu^{2+}$  and a  $Cu^{3+}$  state.

An example of a superconductive compound having a layer-type structure in accordance with the present invention is an oxide of the general composition  $RE_2TMO_4$ , where RE stands for the rare earths (lanthanides) or rare earth-like elements and TM stands for a transition metal. In these compounds the RE portion can be par-

tially substituted by one or more members of the  
alkaline earth group of elements. In these particular  
compounds, the oxygen content is at a deficit.

For example, one such compound that meets this general  
description is lanthanum copper oxide  $\text{La}_2\text{CuO}_4$  in which  
the lanthanum - which belongs to the IIIB group of  
elements - is in part substituted by one member of the  
neighboring IIA group of elements, viz. by one of the  
alkaline earth metals (or by a combination of the mem-  
bers of the IIA group), e.g., by barium. Also, the ox-  
ygen content of the compound can be incomplete such that  
the compound will have the general composition



Another example of a compound meeting this general for-  
15 mula is lanthanum nickel oxide wherein the lanthanum is  
partially substituted by strontium, yielding the general  
formula  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4-y}$ . Still another example is cerium  
nickel oxide wherein the cerium is partially substituted  
by calcium, resulting in  $\text{Ce}_{2-x}\text{Ca}_x\text{NiO}_{4-y}$ .

20 The following description will mainly refer to barium  
as a partial replacement for lanthanum in a  $\text{La}_2\text{CuO}_4$   
compound because it is in the Ba-La-Cu-O system that

many laboratory tests have been conducted. Some compounds of the general Ba-La-Cu-O system have been described by C. Michel and B. Raveau in Rev. Chim. Min. 21 (1984) 407, and by C. Michel, L. Er-Rakho and B. Raveau in Mat. Res. Bull., Vol. 20, (1985) 667-671. They did not, however, find or try to find superconductivity. These references and their teachings regarding perovskite-like layered oxides of mixed valent transition metals, and their preparation, are herein incorporated by reference.

Experiments conducted in connection with the present invention have revealed that high- $T_c$  superconductivity is present in compounds where the rare earth or rare earth-like element is partially replaced by any one or more of the members of the IIA group of elements, i.e., the alkaline earth metals. Actually, the  $T_c$  of  $\text{La}_2\text{CuO}_{4-y}$  with the substitution  $\text{Sr}^{2+}$  is higher and its superconductivity-induced diamagnetism larger than that found with the substitutions  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$ .

The Ba-La-Cu-O system can exhibit a number of crystallographic phases, namely with mixed-valent copper constituents which have itinerant electronic states between non-Jahn-Teller  $\text{Cu}^{3+}$  and Jahn-Teller  $\text{Cu}^{2+}$  ions.

5

This applies likewise to systems where nickel is used in place of copper, with  $Ni^{3+}$  being the Jahn-Teller constituent, and  $Ni^{2+}$  being the non-Jahn-Teller constituent. The existence of Jahn-Teller polarons in conducting crystals was postulated theoretically by K.H. Hoeck, H. Nickisch and H. Thomas in Helv. Phys. Acta 56 (1983) 237. Polarons have large electron-phonon interactions and, therefore, are favorable to the occurrence of superconductivity at higher critical temperatures.

10

Samples in the Ba-La-Cu-O system, when subjected to X-ray analysis, revealed three individual crystallographic phases, viz.

- \* a first layer-type perovskite-like phase, related to the

15

$K_2NiF_4$  structure, with the general composition  $La_{2-x}Ba_xCuO_{4-y}$ , with  $x < 1$  and  $y \geq 0$ ;

20

- \* a second, non-conducting CuO phase; and

\* a third, nearly cubic perovskite phase of the general composition  $La_{1-x}Ba_xCuO_{3-y}$  which appears to be independent of the exact starting composition.

5 Of these three phases the first one appeared to be responsible for the observed high- $T_c$  superconductivity, the critical temperature showing a dependence on the barium concentration in that phase. Obviously, the  $\text{Ba}^{2+}$  substitution caused a mixed-valent state of  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  to preserve charge neutrality. It is assumed that the oxygen deficiency,  $y$ , is the same in the doped and undoped crystallites.

10 In this application, the terms transition metal oxide, copper oxide, Cu-oxide, etc. are meant to broadly include the oxides which exhibit superconductivity at temperatures greater than 26°K. Thus, the term copper oxide can mean, among other things, an oxide such as  $\text{CuO}_{4-y}$  in the mixed oxide composition  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ .

15 Both  $\text{La}_2\text{CuO}_4$  and  $\text{LaCuO}_3$  are metallic conductors at high temperatures in the absence of barium. Actually, both are metals like  $\text{LaNiO}_3$ . Despite their metallic character, the Ba-La-Cu-O type materials are essentially ceramics, as are the other compounds of the  $\text{RE}_2\text{TMO}_4X$  type, and their manufacture generally follows the known principles of ceramic fabrication. The preparation of a superconductive Ba-La-Cu-O compound, for example, in  
20 *hand* *8/17/77*

accordance with the present invention typically involves  
the following manufacturing steps:

\* Preparing aqueous solutions of the respective  
nitrates of barium, lanthanum and copper and  
5 coprecipitation thereof in their appropriate ra-  
tios,

\* adding the coprecipitate to oxalic acid and  
forming an intimate mixture of the respective  
oxalates.

10 \* decomposing the precipitate and causing a solid-  
state reaction by heating the precipitate to a  
temperature between 500 and 1200°C for one to eight  
hours.

15 \* pressing the resulting product at a pressure of  
about 4 kbar to form pellets.

\* re-heating the pellets to a temperature between  
500 and 900°C for one half hour to three hours for  
sintering.

It will be evident to those skilled in the art that if  
the partial substitution of lanthanum by another  
alkaline earth element, such as strontium or calcium,  
is desired, the particular nitrate thereof will have to  
5           be used in place of the barium nitrate of the example  
process described above. Also, if the copper of this  
example is to be replaced by another transition metal,  
the nitrate thereof will obviously have to be employed.  
Other precursors of metal oxides, such as carbonates or  
10           hydroxides, can be chosen in accordance with known  
principles.

Experiments have shown that the partial contents of the  
individual compounds in the starting composition play  
an important role in the formation of the phases present  
15           in the final product. While, as mentioned above, the  
final Ba-La-Cu-O system obtained generally contains the  
said three phases, with the second phase being present  
only in a very small amount, the partial substitution  
of lanthanum by strontium or calcium (and perhaps  
20           beryllium) will result in only one phase existing in the  
final  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$  or  $\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$ , respectively,  
provided  $x < 0.3$ .

With a ratio of 1:1 for the respective (Ba, La) and Cu contents, it is expected that the three phases will occur in the final product. Setting aside the second phase, i.e. the CuO phase whose amount is negligible,  
5 the relative volume amounts of the other two phases are dependent on the barium content in the  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  complex. At the 1:1 ratio and with an  $x = 0.02$ , the onset of a localization transition is observed, i.e., the resistivity increases with decreasing temperature,  
10 and there is no superconductivity.

With  $x = 0.1$  at the same 1:1 starting ratio, there is a resistivity drop at the very high critical temperature of  $35^{\circ}\text{K}$ .

With a (Ba, La) versus Cu ratio of 2:1 in the starting  
15 composition, the composition of the  $\text{La}_2\text{CuO}_4:\text{Ba}$  phase, which appears to be responsible for the superconductivity, is imitated, with the result that now only two phases are present, the CuO phase not existing.  
With a barium content of  $x = 0.15$ , the resistivity drop  
20 occurs at  $T_c = 26^{\circ}\text{K}$ .

The method for preparing these Ba-La-Cu-O sample complexes used two heat treatments for the precipitate at

an elevated temperature for several hours. In the experiments carried out in connection with the present invention it was found that best results were obtained at  $900^{\circ}\text{C}$  for a decomposition and reaction period of 5 hours, and again at  $900^{\circ}\text{C}$  for a sintering period of one hour. These values apply to a 1:1 ratio composition as well as to a 2:1 ratio composition.

For the 2:1 ratio composition, a somewhat higher temperature is permissible owing to the higher melting point of the composition in the absence of excess copper oxide. However, a one-phase compound was not achieved by a high temperature treatment.

Conductivity Measurements (FIGS. 1-4)

The dc conductivity of representative Ba-La-Cu-O compositions was measured to determine their low temperature behavior and to observe their high  $T_c$ . These measurements were performed using the well known four-point probe technique, which is schematically illustrated in FIG. 1. Rectangular shaped samples 10 of

*Exhibit  
8/5/87*  
 $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$  were cut from sintered pellets, and provided with gold sputtered electrodes 12A and 12B, about 0.5 microns thick. Indium wires 14A and 14B contact electrodes 12A and 12B, respectively. The sample was contained in a continuous flow cryostat 16 (Leybold-Heraeus) and measurements were made over a temperature range 300- $412^{\circ}\text{K}$ .

*Amend  
8/5/87*

Electrodes 12A and 12B are connected in a circuit including a current source 18 and a variable resistor 20. Indium leads 22A and 22B are pressed into contact with sample 10 and fixed with silver paint 24. Leads 22A, 22B are connected to a voltage reading instrument 26. Since the current and voltage are accurately determined, the resistivity of the sample 10 is then known. In the configuration used for these measurements, a computer was used to provide a computer-controlled fully-

automatic system for temperature variation, data acquisition and processing.

In FIG. 2, the low temperature dependence of resistivity  
( $\rho$ , measured in ohm-cms) in the composition  
5 *Ba<sub>x</sub>La<sub>5-x</sub>Cu<sub>5</sub>O<sub>5(3-y)</sub>* is plotted for two different values  
of x. For the upper two curves, the value of x(Ba) is  
1 and the left side vertical scale is used. For the  
lower curve, the value of x is 0.75, and the resistivity  
scale on the right hand side of the figure is used. The  
10 data is taken for different values of current density:  
0.25 A/cm<sup>2</sup> for the top curve and 0.50 A/cm<sup>2</sup> for the  
middle and bottom curves.

For barium-doped samples with x(Ba) < 1.0, for example  
with x < 0.3, at current densities of 0.5A/cm<sup>2</sup>, a high-  
15 temperature metallic behavior with an increase in  
resistivity at low temperatures was found as depicted  
in FIG. 2. At still lower temperatures, a sharp drop  
in resistivity (> 90%) occurred which for higher current  
densities became partially suppressed (FIG. 1 upper  
20 curves, left scale). This characteristic drop was  
studied as a function of the annealing conditions, i.e.  
temperature and oxygen partial pressure as shown in FIG.  
2. For samples annealed in air, the transition from

5 itinerant to localized behavior , as indicated by the minimum in resistivity in the 80°K range, was not found to be very pronounced. Annealing in a slightly reducing atmosphere, however, led to an increase in resistivity  
10 and a more pronounced localization effect. At the same time, the onset of the resistivity drop was shifted towards the 30°K region. Curves 4 and 5 (FIG. 3), recorded for samples treated at 900°C, show the occurrence of a shoulder at still lower temperatures, more pronounced  
15 in curve 6. At annealing temperatures of 1040°C, the highly conducting phase has almost vanished. Long annealing times and/or high temperatures will generally destroy the superconductivity.

15 The mixed-valent state of copper is of importance for electron-phonon coupling. Therefore, the concentration of electrons was varied by the Ba/La ratio. A typical curve for a sample with a lower Ba concentration of 0.75 is shown in FIG. 2(right scale). Its resistivity decreases by at least three orders of magnitude, giving  
20 evidence for the bulk being superconducting below 13°K with an onset around 35°K, as shown in FIG. 4 on an expanded temperature scale. FIG. 4 also shows the influence of the current density, typical for granular

compounds. Current densities of 7.5, 2.5, and  $0.5 \text{ A/cm}^2$   
were passed through the superconducting composition.

When cooling the samples from room temperature, the resistivity data first show a metal-like decrease. At low temperatures, a change to an increase occurs in the case of Ca substituted compounds and for the Ba-substituted samples. This increase is followed by a resistivity drop, showing the onset of superconductivity at  $22 \pm 2^\circ\text{K}$  and  $33 \pm 2^\circ\text{K}$  for the Ca and Ba compounds, respectively. In the Sr compound, the resistivity remains metallic down to the resistivity drop at  $40 \pm 1^\circ\text{K}$ . The presence of localization effects, however, depends strongly on alkaline-earth ion concentration and sample preparation, that is to say, on annealing conditions and also on the density, which have to be optimized. All samples with low concentrations of Ca, Sr, and Ba show a strong tendency to localization before the resistivity drops occur.

Apparently, the onset of the superconductivity, i.e. the value of the critical temperature  $T_c$ , is dependent on, among other parameters, the oxygen content of the final compound. It seems that for certain materials, an oxygen deficiency is necessary for the material to have a

high- $T_c$  behavior. In accordance with the present invention, the method described above for making the  $\text{La}_2\text{CuO}_4:\text{Ba}$  complex is complemented by an annealing step during which the oxygen content of the final product can be adjusted. Of course, what was said in connection with the formation of the  $\text{La}_2\text{CuO}_4:\text{Ba}$  compound likewise applies to other compounds of the general formula  $\text{RE}_2\text{THO}_4$  : AE (where AE is an alkaline earth element), such as, e.g.  $\text{Nd}_2\text{NiO}_4:\text{Sr}$ .

In the cases where a heat treatment for decomposition and reaction and/or for sintering was performed at a relatively low temperature, i.e., at no more than  $950^\circ\text{C}$ , the final product is subjected to an annealing step at about  $900^\circ\text{C}$  for about one hour in a reducing atmosphere.

It is assumed that the net effect of this annealing step is a removal of oxygen atoms from certain locations in the matrix of the  $\text{RE}_2\text{THO}_4$  complex, thus creating a distortion in its crystalline structure. The  $\text{O}_2$  partial pressure for annealing in this case may be between  $10^{-1}$  and  $10^{-5}$  bar.

In those cases where a relatively high temperature (i.e., above  $950^\circ\text{C}$ ) is employed for the heat treatment, it might be advantageous to perform the annealing step

in a slightly oxidizing atmosphere. This would make up for an assumed exaggerated removal of oxygen atoms from the system owing to the high temperature and resulting in a too severe distortion of the system's crystalline structure.

Resistivity and susceptibility measurements as a function of temperature of  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ -doped  $\text{La}_2\text{CuO}_{4-y}$  ceramics show the same general tendency as the  $\text{Ba}^{2+}$ -doped samples: a drop in resistivity  $\rho$  ( $T$ ), and a crossover to diamagnetism at a slightly lower temperature. The samples containing  $\text{Sr}^{2+}$  actually yielded a higher onset than those containing  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$ . Furthermore, the diamagnetic susceptibility is about three times as large as for the Ba samples. As the ionic radius of  $\text{Sr}^{2+}$  nearly matches that of  $\text{La}^{3+}$ , it seems that the size effect does not cause the occurrence of superconductivity. On the contrary, it is rather adverse, as the data on  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  indicate.

The highest  $T_c$  for each of the dopant ions investigated occurred for those concentrations where, at room temperature, the  $\text{RE}_{2-x}\text{TM}_x\text{O}_{4-y}$  structure is close to the orthorhombic-tetragonal structural phase transition, which may be related to the substantial electron-phonon

interaction enhanced by the substitution. The  
alkaline-earth substitution of the rare earth metal is  
clearly important, and quite likely creates TM ions with  
no e<sub>g</sub> Jahn-Teller orbitals. Therefore, the absence of  
these Jahn-Teller orbitals, that is, Jahn-Teller holes  
near the Fermi energy, probably plays an important role  
in the T<sub>c</sub> enhancement.

While examples have been given using different transition metal elements in the superconducting compositions,  
copper oxide compositions having mixed valence appear  
to be unique and of particular importance, having  
superconducting properties at temperatures in excess of  
26°K. These mixed valent copper compositions can include a rare earth element and/or a rare earth-like element which can be substituted for by an alkaline earth element. The amount of oxygen in these compositions will vary depending upon the mode of preparation and will be such as to meet the valence requirements of the composition. These copper-based compositions have a layer-like structure, often of a perovskite type. For a more detailed description of some of the types of crystallographic structures that may result, reference is made to the aforementioned publication by Michel and

Raveau in Rev. Chim. Min. 21, 407 (1984), and to C.  
Michel et al., Mat. Res. Bull., Vol. 20, 667-671 (1985).

5 While the invention has been described with respect to particular embodiments thereof, it will be apparent to those of skill in the art that variations can be made therein without departing from the spirit and scope of the present invention. For example, while the range of compositions includes rare earth elements and transition metal elements, the ratios of these elements can be  
10 varied because the crystalline structure can accommodate vacancies of these elements and still retain a layer-like structural phase exhibiting superconductivity.

15 Further, the stoichiometry or degree of non-stoichiometry of oxygen content (i.e., oxygen deficit or surplus) of these compositions can be varied by using reducing or oxidizing atmospheres during formation of the compounds and by using different doping amounts in the rare earth and transition metal sites of the crystal structure. This type of distortion of the crystal  
20 structure and the many forms that it can encompass are readily apparent from reference to the aforementioned Michel and Raveau publications. Thus, the invention broadly relates to mixed (doped) transition metal oxides

having a layer-like structure that exhibit superconducting behavior at temperatures in excess of 26°K. Of these materials, a mixed copper oxide having multivalent states provides high  $T_c$  and favorable superconducting properties.

CLAIMS

Having thus described our invention what we claim as new and desire to secure as Letters Patent, is:

1 2/16/91  
1. A superconductive composition having a transition  
2 temperature greater than 26°K, the composition in-  
3 cluding a rare earth or ~~rare~~ rare earth-like ele-  
4 ment, a transition metal element capable of  
5 exhibiting multivalent states and oxygen, and in-  
6 cluding at least one phase that exhibits  
7 superconductivity at temperature in excess of 26°K.

1  
2. The composition of claim 1, further including an  
3 alkaline earth element substituted for at least one  
4 atom of said rare earth or rare earth-like element  
in said composition.

1  
2. The composition of claim 2, where said transition  
3 metal is Cu.

④ 8/8) → 3

1 4. The composition of claim 3, where said alkaline earth element is selected from the group consisting of  
2 Be  
3 Ca, Ba, and Sr.

1 5. The composition of claim 1, where said transition metal element is selected from the group consisting  
2 of Cu, Ni, and Cr.  
3

1 6. The composition of claim 2, where said rare earth or rare earth-like element is selected from the  
2 group consisting of La, Nd, and Ce.  
3

1 7. The composition of claim 1, where said phase is  
2 crystalline with a perovskite-like structure.

1 8. The composition of claim 2, where said phase is  
2 crystalline with a perovskite-like structure.

1 9. The composition of claim 1, where said phase exhibits  
2 a layer-like crystalline structure.

| 10. The composition of claim 1, where said phase is a  
2 mixed copper oxide phase.

| 11. The composition of claim 1, where said composition  
2 is comprised of mixed oxides with alkaline earth  
3 doping.

| 12. A superconducting combination, including a  
2 superconductive composition having a transition  
3 temperature > 26°K.,

4 means for passing a superconducting electrical  
5 current through said composition while said compo-  
6 sition is at a temperature > 26°K., and

7 cooling means for cooling said composition to a  
8 superconducting state at a temperature in excess  
9 of 26°K.

| 13. The combination of claim 12, where said  
2 superconductive composition includes a transition  
3 metal oxide.

| 14. The combination of claim 12, where said  
2 superconductive composition includes Cu-oxide.

| 15. The combination of claim 12, where said  
2 superconductive composition includes a multivalent  
3 transition metal, oxygen, and at least one addi-  
4 tional element.

| 16. The combination of claim 15, where said transition  
2 metal is Cu.

| 17. The combination of claim 15, where said additional  
2 element is a rare earth or rare earth-like element.

| 18. The combination of claim 15, where said additional  
2 element is an alkaline earth element.

| 19. The combination of claim 12, where said composition  
2 includes a perovskite-like superconducting phase.

1       20. The combination of claim 12, where said composition  
2                   includes a substituted transition metal oxide.

1       21. The combination of claim 20, where said substituted  
2                   transition metal oxide includes a multivalent  
3                   transition metal element.

1       22. The combination of claim 20, where said substituted  
2                   transition metal oxide is an oxide of copper.

1       23. The combination of claim 20, where said substituted  
2                   transition metal oxide has a layer-like structure.

1       24. A method including the steps of forming a transition  
2                   metal oxide having a phase therein which exhibits  
3                   a superconducting state at a critical temperature  
4                   in excess of 26° K,

5       *Maintaining* <sup>is</sup> ~~lowering~~ the temperature of said material at <sup>a temperature less than</sup> ~~[least]~~  
6                   to] said critical temperature to produce said  
7                   superconducting state in said phase, and

8       passing an electrical supercurrent through said  
9       transition metal oxide while it is in said super-  
10      conducting state.

1   25. The method of claim 24, where said transition metal  
2       oxide is comprised of a transition metal capable  
3       of exhibiting multivalent states.

1   26. The method of claim 24, where said transition metal  
2       oxide is comprised of a Cu oxide.

1   27. A superconducting composition having a transition  
2       temperature in excess of 26°K, said composition  
3       being a substituted Cu-oxide including a supercon-  
4       ducting phase having a structure substantially  
5       close to the orthorhombic-tetragonal phase transi-  
6       tion of said composition.

1   28. The composition of claim 27, where said substituted  
2       Cu-oxide includes a rare earth or rare earth-like  
3       element.

1 29. The composition of claim 27, where said substituted  
2 Cu-oxide includes an alkaline earth element.

1 30. The composition of claim 29, where said alkaline  
2 earth element is atomically large with respect to  
3 Cu.

1 31. The composition of claim 27, where said composition  
2 has a crystalline structure which enhances  
3 electron-phonon interactions to produce  
4 superconductivity at a temperature in excess of  
5 26°K.

A.Y  
Amendment  
2/8/91

1 32. The composition of claim 31, where said crystalline  
2 structure is layer-like, enhancing the number of  
3 Jahn-Teller polarons in said composite? --composition--

1 33. A superconducting composition having a supercon-  
2 ducting onset temperature in excess of 26°K., the  
3 composition being comprised of a copper oxide doped  
4 with an alkaline earth element where the concen-

5 tration of said alkaline earth element is near to  
6 the concentration of said alkaline earth element  
7 where the superconducting copper oxide phase in  
8 said composition undergoes an orthorhombic to  
9 tetragonal structural phase transition.

| 34. A superconducting composition having a supercon-  
2 ducting onset temperature in excess of 26°K, the  
3 composition being comprised of a mixed copper oxide  
4 doped with an element chosen to create Cu<sup>3+</sup> ions  
5 in said composition.

| 35. The composition of claim 34, where said doping el-  
2 ement includes an alkaline earth element.

| 36. A combination comprising:

2 a composition having a superconducting onset tem-  
3 perature in excess of 26°K, said composition being  
4 comprised of a substituted copper oxide exhibiting  
5 mixed valence states and at least one other element  
6 in its crystalline structure,

7 means for passing a superconducting electrical  
8 current through said composition while said compo-  
9 sition is at a temperature in excess of 26°K ~~and~~.

10 cooling means for cooling said composition to a  
11 superconducting state at a temperature in excess  
12 of 26°K }  
{

1 37. The combination of claim 36, where said at least  
2 one other element is an alkaline earth element.

1 38. The combination of claim 36, where said at least  
2 one other element is an element which creates Cu<sup>3+</sup>  
3 ions in said composition.

1 39. The composition of claim 36, where said at least  
2 one other element is an element chosen to create  
3 the presence of both Cu<sup>2+</sup> and Cu<sup>3+</sup> ions in said  
4 composition.

1      40. A superconductor exhibiting a superconducting onset  
2                at a temperature in excess of 26°K, said supercon-  
3                ductor being comprised of at least four elements,  
4                none of which is itself superconducting.

1      41. The superconductor of claim 40, where said elements  
2                include a transition metal and oxygen.

1      42. A superconductor having a superconducting onset  
2                temperature greater 26°K, said superconductor being  
3                a doped transition metal oxide, where said transi-  
4                tion metal is itself non-superconducting.

1      43. The superconductor of claim 42, where said doped  
2                transition metal oxide is multivalent in said  
3                superconductor.

1      44. The superconductor of claim 42, further including  
2                an element which creates a mixed valent state of  
3                said transition metal.

1 45. The superconductor of claim 43, where said transi-  
2 tion metal is Cu.

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1 46. A superconductor having a superconducting onset  
2 temperature greater than 26°K, said superconductor  
3 being an oxide having multivalent oxidation states  
4 and including a metal, said oxide having a crys-  
5 talline structure which is oxygen deficient.

1 47. The superconductor of claim 46, where said transi-  
2 tion metal is Cu.

1 48. A superconductive composition comprised of a tran-  
2 sition metal oxide having substitutions therein,  
3 the amount of said substitutions being sufficient  
4 to produce sufficient electron-phonon interactions.  
5 in said composition that said composition exhibits  
6 a superconducting onset at temperatures greater  
7 than 26°K.

1    49. The composition of claim 48, where said transition  
2       metal oxide is multivalent in said composition.

1    50. The composition of claim 48, where said transition  
2       metal is Cu.

1    51. The composition of claim 48, where said substi-  
2       tutions include an alkaline earth element.

1    52. The composition of claim 48, where said substi-  
2       tutions include a rare earth or rare earth-like  
3       element.

1    53. A superconductor comprised of a copper oxide having  
2       a layer-like crystalline structure and at least one  
3       additional element substituted in said crystalline  
4       structure, said structure being oxygen deficient  
5       and exhibiting a superconducting onset temperature  
6       in excess of 26°K.

1        54. The superconductor of claim 53, where said addi-  
2        tional element creates a mixed valent state of said  
3        copper oxide in said superconductor.

1        55. A combination, comprising:

2        a transition metal oxide having an oxygen defi-  
3        ciency, said transition metal being non-  
4        superconducting and said oxide having multivalent  
5        states,

6        means for passing an electrical superconducting  
7        current through said oxide while said oxide is at  
8        a temperature greater than  $26^{\circ}\text{K}$ , and  
8(47)

9        cooling means for cooling said oxide in a super-  
10      conducting state at a temperature greater than  
11       $26^{\circ}\text{K}$

1        56. The combination of claim 55, where said transition  
2        metal is Cu.

1      57. A combination including;

2      a superconducting oxide having a superconducting onset  
3      temperature in excess of 26°K and containing at least 3  
4      non-superconducting elements,

5      means for passing a supercurrent through said oxide  
6      while said oxide is maintained at a temperature greater  
7      than 26°K, and

8      means for maintaining said oxide in a superconducting  
9      state at a temperature greater than 26°K.

1      58. A combination, comprised of:

2      a copper oxide superconductor including an element which  
3      creates a mixed valent state in said oxide, said oxide  
4      being crystalline and having a layer-like structure,

5      means for passing a supercurrent through said copper  
6      oxide while it is maintained at a temperature greater  
7      than 26°K, and

*6 8* 8 means for [cooling] <sup>maintaining</sup> said copper oxide (to) a superconductive  
*8 9* state at a temperature greater than 26°K.

*1* 59. A combination, comprised of:

*2* a superconducting ceramic-like material having an  
*3* onset of superconductivity at a temperature in ex-  
*4* cess of 26°K.,

*5* means for passing a supercurrent through said  
*6* superconducting ceramic-like material while said  
*7* ceramic-like material is maintained at a temper-  
*8* ature in excess of 26°K., and

*9* *8/10* 9 means for [cooling] <sup>maintaining</sup> said superconducting ceramic-like  
*10* material <sup>in</sup> to a superconductive state at a temper-  
*11* ature greater than 26°K.

*1* 60. A superconductor comprised of a transition metal  
*2* oxide, and at least one additional element, said  
*3* superconductor having a distorted crystalline  
*4* structure characterized by an oxygen deficiency and

5 exhibiting a superconducting onset temperature in  
6 excess of 26°K.

1 61. The superconductor of claim 60, where said transi-  
2 tion metal is Cu.

1 62. A superconductor comprised of a transition metal  
2 oxide and at least one additional element, said  
3 superconductor having a distorted crystalline  
4 structure characterized by an oxygen excess and  
5 exhibiting a superconducting onset temperature in  
6 excess of 26°K.

1 63. The superconductor of claim 62, where said transi-  
2 tion metal is Cu.

1 64. A combination, comprising:

2 a mixed copper oxide composition having enhanced  
3 polaron formation, said composition including an  
4 element causing said copper to have a mixed valent

*Ansel  
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1/81*

5 state in said composition, said composition further  
6 having a distorted octahedral oxygen environment  
7 leading to a  $T_c$  greater than 26°K.,  
  
8 means for providing a supercurrent through said  
9 composition at temperatures greater than 26°K. [and--  
10 cooling means for cooling said composition to a  
11 temperature greater than 26°K.]

1 65. A superconducting composition exhibiting  
2 superconductivity at temperatures greater than  
3 26°K, said composition being a ceramic-like mate-  
4 rial in the RE-AE-TM-O system, where RE is a rare  
5 earth or near rare earth element, AE is an alkaline  
6 earth element, TM is a multivalent transition metal  
7 element having at least two valence states in said  
8 composition, and O is oxygen, the ratio of the  
9 amounts of said transition metal in said two va-  
10 lence states being determined by the ratio RE : AE.

/ 66. A superconductive composition having a transition  
2 temperature greater than 26°K, the composition in-

3       cluding a multivalent transition metal oxide and  
4       at least one additional element, said composition  
5       having a distorted orthorhombic crystalline struc-  
6       ture.

1       67. The composition of claim 66, where said transition  
2       metal oxide is a mixed copper oxide.

1       68. The composition of claim 67, where said one addi-  
2       tional element is an alkaline earth element.

1       69. A superconductive combination, comprising:

2       a superconducting composition exhibiting a super-  
3       conducting transition temperature greater than  
4       26°K, said composition being a transition metal  
5       oxide having a distorted orthorhombic crystalline  
6       structure, and

7       means for passing a superconducting electrical  
8       current through said composition while said compo-  
9       sition is at a temperature greater than 26°K.

1    70. The combination of claim 69, where said transition  
2    metal oxide is a mixed copper oxide.

1    71. The combination of claim 70, where said mixed copper  
2    oxide includes an alkaline earth element.

1    72. The combination of claim 71, where said mixed copper  
2    oxide further includes a rare earth or rare earth-  
3    like element.

1    73. A method for making a superconductor having a  
2    superconducting onset temperature > 26°K, said  
3    method including the steps of:

4       preparing powders of oxygen-containing compounds  
5       of a rare earth or rare earth-like element, an  
6       alkaline earth element, and copper,

7       mixing said compounds and firing said mixture to  
8       create a mixed copper oxide composition including  
9       said alkaline earth element and said rare earth or  
10      rare earth-like element, and

11 annealing said mixed copper oxide composition at  
12 an elevated temperature less than about 950°C in  
13 an atmosphere including oxygen to produce a super-  
14 conducting composition having a mixed copper oxide  
15 phase exhibiting a superconducting onset temper-  
16 ature greater than 26°K, said superconducting com-  
17 position having a layer-like crystalline structure  
18 after said annealing step.

1 74. The method of claim 73, where the amount of oxygen  
2 incorporated into said composition is adjusted by  
3 said annealing step, the amount of oxygen therein  
4 affecting the critical temperature  $T_c$  of the  
5 superconducting composition.

1 75. A method for making a superconductor having a  
2 superconducting onset temperature greater than  
3 26°K, said superconductor being comprised of a rare  
4 earth or rare earth-like element (RE), an alkaline  
5 earth element (AE), copper (CU), and oxygen (O) and  
6 having the general formula RE-AE-CU-O, said method  
7 including the steps of combining said rare earth  
8 or rare earth-like element, said alkaline earth

9 element and said copper in the presence of oxygen  
10 to produce a mixed copper oxide including said rare  
11 earth or rare earth-like element and said alkaline  
12 earth element therein, and  
  
13 heating said mixed copper oxide to produce a  
14 superconductor having a crystalline layer-like  
15 structure and exhibiting a superconducting onset  
16 temperature greater than 26°K, the critical tran-  
17 sition temperature of said superconductor being  
18 dependent on the amount of said alkaline earth el-  
19 ement therein.

1 76. The method of claim 75, where said heating step is  
2 done in an atmosphere including oxygen.

1 77. A combination, comprising:

2 a mixed copper oxide composition including an  
3 alkaline earth element (AE) and a rare earth or  
4 rare earth-like element (RE), said composition  
5 having a layer-like crystalline structure and  
6 multi-valent oxidation states, said composition

*Answer  
b  
9/87*

7 exhibiting a substantially zero resistance to the flow of electrical current therethrough when cooled to a superconducting state at a temperature in excess of 26°K, and

11 electrical means for passing an electrical super-current through said composition when said composition exhibits substantially zero resistance at a temperature greater than 26°K.

12

13

14

1 78. The combination of claim 77, where the ratio  
2 ( $\Delta E$ , RE) : Cu is substantially 1:1.

*Answer  
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9/87*

1 79. The combination of claim 77, where the ratio  
2 ( $\Delta E$ , RE) : Cu is substantially 2:1.

1 80. The combination of claim 77, where said crystalline  
2 structure is perovskite-like.

1        81. The combination of claim 77, where said mixed copper  
2              oxide composition has a non-stoichiometric amount  
3              of oxygen therein.

1        82. A method for making a superconductor having a  
2                  superconducting onset temperature greater than 26°,  
3                  said superconductor being comprised of a rare earth  
4                  or rare earth-like element (RE), an alkaline earth  
5                  element (AE), a transition metal element (TM), and  
6                  oxygen (O) and having the general formula  
7                  RE-AE-TM-O, said method including the steps of  
8                  combining said rare earth or rare earth-like ele-  
9                  ment, said alkaline earth element and said transi-  
10                 tion metal element in the presence of oxygen to  
11                 produce a mixed transition metal oxide including  
12                 said rare earth or rare earth-like element and said  
13                 alkaline earth element therein, and

14 heating said mixed transition metal oxide to  
15 produce a superconductor having a crystalline  
16 layer-like structure and exhibiting a supercon-  
17 ducting onset temperature greater than 26°K, said  
18 superconductor having a non-stoichiometric amount  
19 of oxygen therein.

1        83. The method of claim 82, where said transition metal  
2                  is copper.

1        84. A superconducting combination, comprising:

2                  a mixed transition metal oxide composition con-  
3                  taining a non-stoichiometric amount of oxygen  
4                  therein, a transition metal and at least one addi-  
5                  tional element, said composition having substan-  
6                  tially zero resistance to the flow of electricity  
7                  therethrough when cooled to a superconducting state  
8                  at a temperature greater than 26°K, and  
  
9                  electrical means for passing an electrical super-  
10                  current through said composition when said compo-  
11                  sition is in said superconducting state at a  
12                  temperature greater than 26°K.

1        85. The combination of claim 84, where said transition  
2                  metal is copper.

1        86. A method, comprising the steps of:

2 forming a composition including a transition metal,  
3 a rare earth or rare earth-like element, an  
4 alkaline earth element, and oxygen, where said  
5 composition is a mixed transition metal oxide hav-  
6 ing a non-stoichiometric amount of oxygen therein  
7 and exhibiting a superconducting state at a tem-  
8 perature greater than 26°K,

*around*  
*6*  
*8(1)* 9 *containing* [cooling] said composition [to] said superconducting  
10 state at a temperature greater than 26°K, and

11 passing an electrical current through said compo-  
12 sition while said composition is in said supercon-  
13 ducting state.

1 87. The method of claim 86, where said transition metal  
2 is copper.

1 88. A method, including the steps of:

2 forming a composition exhibiting a superconductive  
3 state at a temperature in excess of 26°K,

111

4

<sup>Maintaining</sup> [Cooling] said composition [to] a temperature in excess

5

of 26°K at which temperature said composition ex-

6

hibits said superconductive state, and

7

passing an electrical current through said compo-

8

sition while said composition is in said

9

superconductive state.

1 89. The method of claim 88, where said composition is  
2 comprised of a metal oxide.

1 90. The metal of claim 88, where said composition is  
2 comprised of a transition metal oxide.

FIG. 1

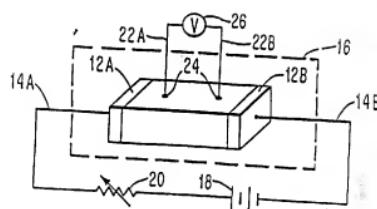


FIG. 2

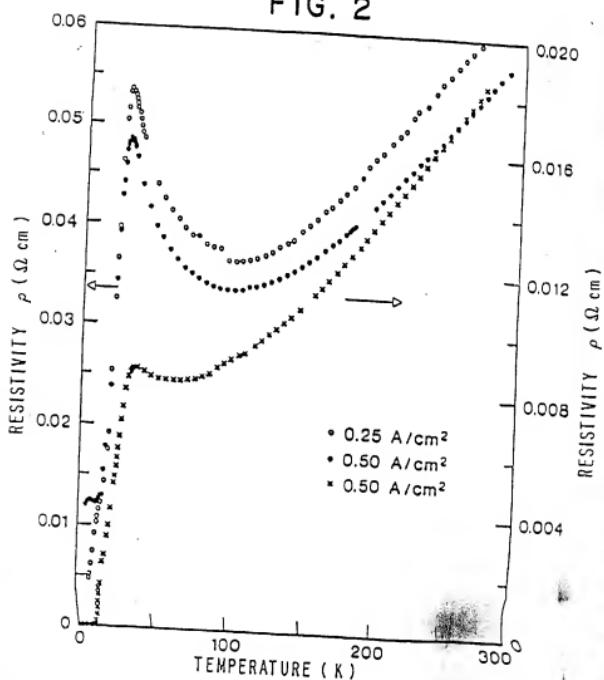
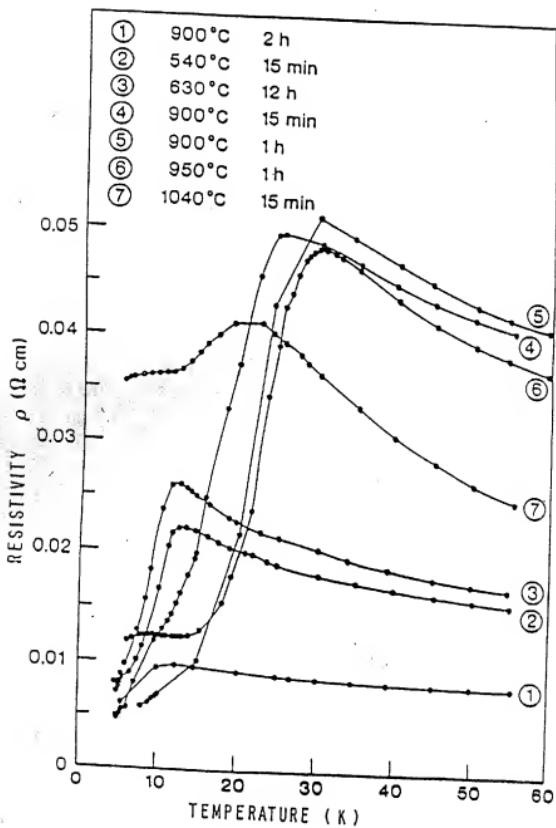
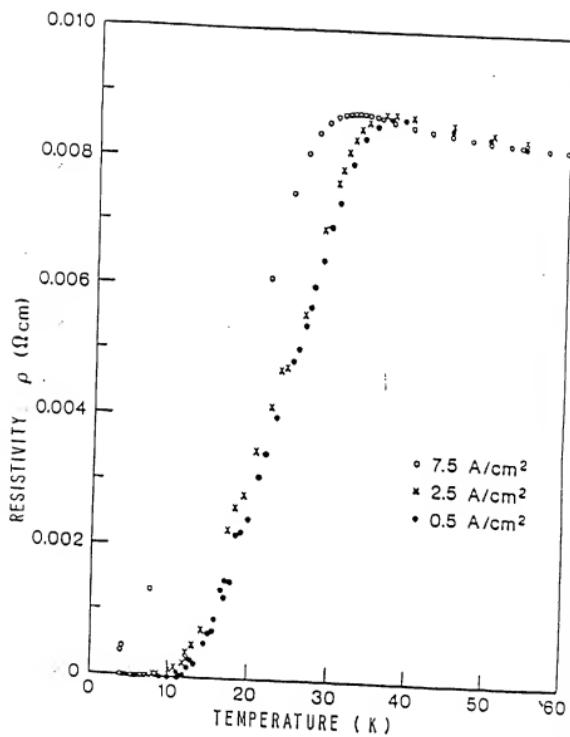


FIG. 3



3/3  
Y09-87-074X

FIG. 4



**BRIEF ATTACHMENT AV**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 6**

AN

## 超伝導の新材料を発見

બાળ

セラミックス  
“高温”でも  
十分な働き

from ASAHI SHINKUN

International Satellite Edition  
28. 11. 1986 (London)

## DISCOVERY OF NEW SUPERCONDUCTING MATERIAL

" CERAMIC WITH SUFFICIENT SUPERCONDUCTIVE POWER IN  
HIGH TEMPERATURE REGION "

A new ceramic with a very high  $T_c$  of 30K of the superconducting transition has been found. The possibility of high  $T_c$  - superconductivity has been reported by scientists in Switzerland in this spring. The group of Prof. Shoji TANAKA, Dept. Appl.Phys., Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.  $T_c$ 's of all superconducting materials which we have in practical application till now are lower than 20K. Therefore we need large amount of liquid He for cooling. Note that the price of liquid He is very expensive. But with this new material we can use cheaper liquid  $H_2$  for cooling. We can expect great from this material to the applications such as linear motorcars, electricity transport systems, etc.

The ceramic newly discovered, is an oxide compound of La and Cu with Ba, which has a structure of the so-called perovskite and shows metal-like properties. Prof. Tanaka's laboratory confirmed that this material shows diamagnetism (Meissner effect) up to 30K, which is the most important indication of the existence of superconductivity.

There are a lot of possibilities for practical applications of superconductors. For example very strong magnets, made of superconducting coils,etc. But one handicap is that  $T_c$  is too low in each material we know till now.

The  $T_c$  of Nb-alloys which are already in practical use are lower than 20K. The record of  $T_c$  in a laboratory is around 23.2K. This record has not been broken since 1973.

Nowadays each instrument using superconductors is operated by liquid He cooling, and He is a very rare material with a boiling point of 4K. Liquid He used in present Japan is exclusively imported from the USA. If we could get a material with a high  $T_c$  of 30K, we can not only use liquid  $H_2$  but also liquid Ne with a boiling point of 27K.

Since the application of superconductors to many fields, such as very strong magnets, medical use of NMR machines,etc. show rapid increasing, research field of high  $T_c$  superconductivity is highly competitive all over the world.

**BRIEF ATTACHMENT AW**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Date: March 1, 2004

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

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For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 23**

AW

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# COPPER OXIDE SUPERCONDUCTORS

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Timir Datta  
Horacio A. Farach

*with help from*

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"A Wiley-Interscience publication."

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A2

## PREFACE

The unprecedented worldwide effort in superconductivity research—that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. The time is now ripe to bring together in one place the results of this research effort so that scientists working in this field can better acquire an overall perspective, and at the same time have available in one place a collection of detailed experimental data. This volume reviews the experimental aspects of the field of oxide superconductivity with transition temperatures from 30 K to above 120 K, from the time of its discovery by Bednorz and Müller in April 1986 until a few months after the award of the Nobel Prize to them in October 1987. During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as  $\text{BiSrCaCuO}$ ,  $\text{LaSrCuO}$ ,  $\text{TlBaCaCuO}$ , and  $\text{YBa-CuO}$  has emerged. At the same time there has been a continual debate on the extent to which the BCS theory and the electron-phonon interaction mechanism apply to the new materials, and new theoretical models are periodically proposed. We discuss these matters and, when appropriate, make comparisons with transition metal and other previously known superconductors. Many of the experimental results are summarized in figures and tables.

The field of high-temperature superconductivity is still evolving, and some ideas and explanations may be changed by the time these notes appear in print. Nevertheless, it is helpful to discuss them here to give insights into work now in progress, to give coherence to the present work, and to provide guidance for future work. It is hoped that in the not too distant future the field will settle down enough to permit a more definitive monograph to be written.

The literature has been covered almost to the end of 1987, and some 1988 work has been discussed. This has been an enormous task, and we apologize for any omissions in the citing and discussion of articles.

We wish to thank the following for giving us some advanced notice about their work: R. Barrio, B. Battlogg, L. A. Boatner, G. Burns, J. Drumheller, H. Enomoto, P. K. Gallagher, R. Goldfarb, J. E. Graebner, R. L. Greene, J. Heremans, T. C. Johnson, J. K. Karamas, M. Levy, J. W. Lynn, A. Malozemoff, K. A. Müller, T. Nishino, N. Nucker, J. C. Phillips, R. M. Silver, G. Shirane, J. Stankowski, B. Stridzker, S. Tanigawa, G. A. Thomas, and W. H. Weber. We appreciate comments on the manuscript from S. Alterowitz, C. L. Chien, D. K. Finnamore, J. Goodenough, J. R. Morton, and C. Uher, and helpful discussions with J. Budnick, M. H. Cohen, M. L. Cohen, R. Creswick, S. Deb, M. Fluss, A. Freeman, D. U. Gubser, A. M. Hermann, V. Z. Kresin, H. Ledbetter, W. E. Pickett, M. Tinkham, C. E. Violet, and S. A. Wolf. Support from the University of South Carolina, the Naval Research Laboratory, and the National Science Foundation Grant ISP 80 11451 is gratefully acknowledged.

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TIMIR DATTA  
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*Columbia, South Carolina  
July 1988*

A4

ects of the BCS theory, however,

and detailed treatment of the properties see the extent to which they can agree with some of the other in these two chapters.

# V

## PREPARATION AND CHARACTERIZATION OF SAMPLES

### A. INTRODUCTION

Copper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials. Nevertheless, it should be emphasized that the preparation of these samples does involve some risks since the procedures are carried out at quite high temperatures, often in oxygen atmospheres. In addition, some of the chemicals are toxic, and in the case of thallium compounds the degree of toxicity is extremely high so ingestion, inhalation, and contact with the skin must be prevented.

The superconducting properties of the copper oxide compounds are quite sensitive to the method of preparation and annealing. Multiphase samples containing fractions with  $T_c$  above liquid nitrogen temperature (Monoc) can be synthesized using rather crude techniques, but really high-grade single-phase specimens require careful attention to such factors as temperature control, oxygen content of the surrounding gas, annealing cycles, grain sizes, and pelletizing procedures. The ratio of cations in the final sample is important, but even more critical and more difficult to control is the oxygen content. However, in the case of the Bi- and Tl-based compounds, the superconducting properties are less sensitive to the oxygen content.

Figure V-1 illustrates how preparation conditions can influence superconducting properties. It shows how the calcination temperature, the annealing time, and the quenching conditions affect the resistivity drop at  $T_c$  of a BiSrCa-CuO pellet, a related copper-enriched specimen, and an aluminum-doped coun-

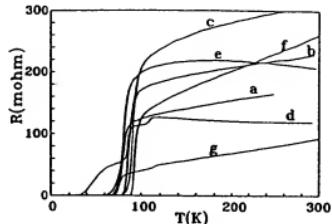


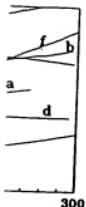
Fig. V-1. Effects of heat treatments on the resistivity transition of  $\text{BiSrCaCuO}_{4-x}$  (d) calcined at 860°C, (b) calcined at 885°C, (c) calcined at 901°C, (d) aluminum-doped sample calcined at 875°C, prolonged annealing, (e) copper-rich sample calcined at 860°C, (f) aluminum-doped sample calcined at 885°C, slow quenching and (g) calcined at 885°C, prolonged annealing, and slow quenching (Chuz5).

terpart (Chuz5). These samples were all calcined and annealed in the same temperature range and air-quenched to room temperature.

Polycrystalline samples are the easiest to prepare, and much of the early work was carried out with them. Of greater significance is work carried out with thin films and single crystals, and these require more specialized preparation techniques. More and more of the recent work has been done with such samples.

Many authors have provided sample preparation information, and others have detailed heat treatments and oxygen control. Some representative techniques will be discussed.

The beginning of this chapter will treat methods of preparing bulk superconducting samples in general, and then samples of special types such as thin film and single crystals. The remainder of the chapter will discuss ways of checking the composition and quality of the samples. The thermodynamic or subsolidus phase diagram of the ternary  $\text{Y}-\text{Ba}-\text{Cu}$  oxide system illustrated in Fig. V-2 contains several stable stoichiometric compounds such as the end-point oxide  $\text{Y}_2\text{O}_3$ ,  $\text{Ba}_2\text{O}$ , and  $\text{CuO}$  at the apices, the binary oxides stable at 950°,  $(\text{Ba}_2\text{CuO}_3)$ ,  $\text{Ba}_2\text{CuO}_5$ ,  $\text{BaCuO}_2$ ,  $\text{Y}_2\text{Cu}_3\text{O}_5$ ,  $\text{Y}_2\text{Ba}_3\text{O}_7$ ,  $\text{Y}_2\text{Ba}_4\text{O}_7$ , along the edges, and ternary oxides such as  $(\text{YBa}_2\text{Cu}_3\text{O}_7)$ , the semiconducting green phase  $\text{Y}_2\text{Ba}_3\text{Cu}_3\text{O}_9$ , and the superconducting black solid  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in the interior (Beye2, Bour3, Capo1, Eagl1, Frase, Hosoy, Jone1, Kaise, Kurth, Kuzz Leez3, Lian1, Mal11, Schn1, Schu1, Takay, Torra, Wagne). Compounds in parentheses are not on the figure, but are reported by other workers. The existence of a narrow range of solid solution was reported (Panso), and this was argued against (Wagne) by the same group.



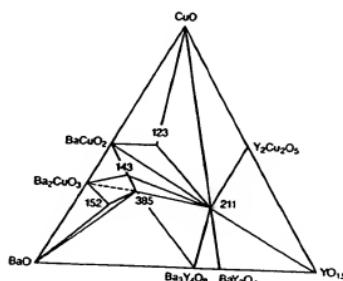
transition of BiSrCaCuO<sub>7- $\delta$</sub>  (*a*) at 901°C, (*d*) aluminum-doped copper-rich sample calcined at slow quenching and (*g*) calcined (25).

annealed in the same tem-  
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nd much of the early work work carried out with thin cialized preparation tech- lone with such samples.

information, and others some representative tech-

preparing bulk superconducting types such as thin films discuss ways of checking modynamic or solidus illustrated in Fig. V-2 consists as the end-point oxides table at 950°,  $(\text{Ba}_3\text{CuO}_4)$ , and  $(\text{Y}_2\text{Ba}_4\text{O}_7)$ , along the incongruent melting green phase  $\text{a}_2\text{Cu}_3\text{O}_{7-4}$  in the interior, Kaise, Kurth, Kuzz, ra, Wagne). Compounds by other workers. The orted (Panso) and then



Compound	Slowly cooled to room temperature
123 - $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$	O <sub>7</sub>
143 - $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$	O <sub>9</sub>
385 - $\text{YBa}_2\text{Cu}_3\text{O}_{12.5+\delta}$	O <sub>18</sub>
152 - $\text{YBa}_2\text{Cu}_3\text{O}_{5.5+\delta}$	O <sub>9</sub>
211 - $\text{Y}_2\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$	O <sub>23</sub>

**Fig. V-2.** Ternary phase diagram of the  $\text{Y}_2\text{O}_3$ - $\text{BaO}$ - $\text{CuO}$  system at 950°C. The green phase [ $\text{Y}_2\text{BaCuO}_5$ , (211)] the superconducting phase [ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , (123)], and three other compounds are shown in the interior of the diagram (Delso).

## B. METHODS OF PREPARATION

In this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hafsi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical processes involved in the transformation of a mixture of compounds into a superconductor. The coprecipitation technique mixes the constituents on an atomic scale and forms fine powders, but it requires careful control of the pH and some familiarity with analytical chemistry. The sol-gel procedure requires more competence in analytical procedures.

In the solid-state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates, or carbonates of Ba, Bi, La, Sr, Ti, Y, or other elements. Sometimes nitrates are formed first by dissolving oxides in nitric acid and decomposing the solution at 500°C before calcination.

(e.g., Davis, Holla, Kelle). These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcining for an extended period (= 20 hr) at elevated temperatures ( $\approx 900^{\circ}\text{C}$ ). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step. As the reaction proceeds, the color of the charge changes. The process usually ends with a final oxygen anneal followed by a slow cool down to room temperature of the powder, or pellets made from the powder, by sintering in a cold or hot press. Sintering is not essential for the chemical process, but for transport and other measurements it is convenient to have the material pelletized. A number of researchers have provided information on this solid-state reaction approach (e.g., Allge, Finez, Galla, Garla, Gopal, Gubse, Hajki, Hatan, Herrm, Hikal, Hirab, Jayar, Maenl, Mood1, Mood2, Neume, Poeppe, Polle, Qadri, Rhyne, Ruzic, Saito, Sait1, Sawal, Shamo, Takit, Tothz, Wuzz3).

Some of the earlier works on foils, thick films, wires, or coatings employed a suspension of the calcined powder in a suitable organic binder, and the desired product was obtained by conventional industrial processes such as extruding, spraying, or coating.

In the second or coprecipitation process the starting materials for calcination are produced by precipitating them together from solution (e.g., Asela, Bedno, Leez7, Wang2). This has the advantage of mixing the constituents on an atomic scale. In addition the precipitates may form fine powders whose uniformity can be controlled, which can eliminate some of the labor. Once the precipitate has been dried, calcining can begin as in the solid-state reaction procedure. A disadvantage of this method, at least as far as the average physicist or materials scientist is concerned, is that it requires considerable skill in chemical procedures.

Another procedure for obtaining the start-up powder is the sol-gel technique in which an aqueous solution containing the proper ratios of Ba, Cu, and Y nitrates is emulsified in an organic phase and the resulting droplets are gelled by the addition of a high-molecular-weight primary amine which extracts the nitric acid. This process was initially applied to the La materials, but has been perfected for  $\text{YBaCuO}$  as well (Cimaz, Hafii).

When using commercial chemical supplies to facilitate the calcination process a dry or wet (acetone) pregrinding with an agate mortar and pestle or a ball mill is recommended. Gravimetric amounts of the powdered precursor materials are thoroughly mixed and placed in a platinum or ceramic crucible. Care must be taken to ensure the compatibility of the ceramic crucible with the chemicals to obviate reaction and corrosion problems.

Complete recipes for the  $\text{YBa}_2$  material have been described (e.g., Gran2). Typically, the mixture of unreacted oxides is calcined in air or oxygen around  $900^{\circ}\text{C}$  for 15 hr. During this time the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  mixture changes color from the green  $\text{Y}_2\text{Ba}_2\text{Cu}_3\text{O}_8$  phase to the dark gray  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound. Then the charge is taken out, crushed, and scanned with X rays to determine its purity. If warranted by the powder pattern X-ray scan, the calcination process is repeated. Often, at this stage the material is very oxygen poor, and electrically it is semi-